

Cellulose Acetate-Al₂O₃ Hybrid Material Coated with N-Propyl-1,4-diazabicyclo [2.2.2] Octane Chloride. Preparation, Characterization and Study of Some Metal Halides Adsorption from Ethanol Solution

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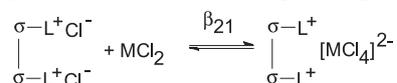
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A preparação, bem como as propriedades de adsorção de MCl_n (M=Fe(III), Co(II) e Cu(II)) de soluções etanólicas são descritas para um novo material híbrido acetato de celulose /Al₂O₃ recoberto com cloreto de N-propil-1,4 diazabicyclo [2.2.2] octano. A diamina está ligada à superfície do acetato de celulose/Al₂O₃ pela ligação covalente Al-O-Si e então, o material obtido é quimicamente muito estável e apresenta elevada capacidade de adsorção de MCl_n de solução etanólica. Quando o material (designado como σ-L⁺Cl⁻) entra em contacto com soluções do haleto metálico, os sais difundem na interface substrato-solução como espécies neutras e são fixadas na forma de complexos aniônicos. Estes são presos à superfície devido às interações eletrostáticas com a carga positiva dos centros ~L⁺. As capacidades de adsorção do material (t, em mmol g⁻¹) e as duas afinidades pelo haleto metálicos foram determinadas analisando-se as isotermas de adsorção com o auxílio de um modelo de centros polidentados fixos. As constantes de equilíbrio da adsorção (β, em mmol L⁻¹) foram usadas como características de afinidade. Para o FeCl₃, ao equilíbrio de adsorção

$$\sigma-L^+Cl^- + FeCl_3 \xrightleftharpoons{\beta_{11}} \sigma-L^+[FeCl_4]^-$$

a concentração específica dos centros de adsorção t_{σ-L⁺Cl⁻} é igual a 1,42 e 0,115; log β₁₁ = 3,14. A adsorção de CoCl₂ e CuCl₂ (MCl₂) é descrita de uma forma mais complexa:

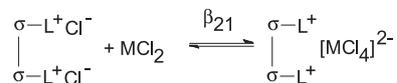


Os seguintes valores dos parâmetros foram obtidos: t_{(σ-L⁺Cl⁻)₂} = 0,20 e 0,115; log β₂₁ = 4,08 e 3,3, respectivamente para CoCl₂ e CuCl₂.

The preparation, characterization as well as the adsorption properties of MCl_n (M= Fe(III), Co(II) and Cu(II)) from ethanol solutions by the new hybrid material cellulose acetate /Al₂O₃ coated with N-propyl-1,4 diazabicyclo [2.2.2] octane chloride group are described. The diamine is bonded to the cellulose acetate /Al₂O₃ surface by Al-O-Si covalent bonds and thus, the material obtained is chemically very stable and shows high adsorption capacity in adsorbing MCl_n from ethanol solutions. When the material (designated as σ-L⁺Cl⁻) comes into contact with the metal halide solutions, the salts diffuse into the substrate-solution interface as neutral species and are fixed in the form of the anionic complexes. The latter are held near the surface due to the electrostatic interactions with the positively charged centers ~L⁺. The adsorption capacities of the material (t, in mmol g⁻¹) and its affinities to the metal halides were determined by analyzing the adsorption isotherms with the help of the model of fixed polydentate centers. The constants of the adsorption equilibria (β, in L mol⁻¹) were used as the quantitative characteristics of affinity. For the FeCl₃ adsorption equilibrium

$$\sigma-L^+Cl^- + FeCl_3 \xrightleftharpoons{\beta_{11}} \sigma-L^+[FeCl_4]^-$$

the specific concentration of the sorption centers t_{σ-L⁺Cl⁻} is equal to 1.42 and log β₁₁ = 3.14. The adsorption of CoCl₂ and CuCl₂ (MCl₂) is described in a more complicated way:



The following values of parameters were obtained: t_{(σ-L⁺Cl⁻)₂} = 0.20 and 0.115; log β₂₁ = 4.08 and 3.3 for CoCl₂ and CuCl₂ respectively.

Keywords: N-propyl-1,4-diazabicyclo [2.2.2] octane chloride, Al₂O₃ coated cellulose acetate, chemically modified cellulose acetate, metal halide adsorption, heterogeneous equilibrium constant

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Introduction

Cellulose and cellulose acetate are frequently used to prepare composite materials since they present many intrinsic advantages such as low cost, availability, biodegradability and easy handling.¹ In native form they show good thermal stability up to 473 K and a high chemical resistance to treatment with almost all commonly used solvents. The polymer is relatively inert because the hydroxyl groups, which are responsible for the majority of the reactions with organic and inorganic reagents, are involved into inter- and intramolecular hydrogen bonding.^{2,3}

In order to make cellulose acetate more reactive, the surface modified composites have been prepared with many metal oxides such as TiO₂,^{4,5} ZrO₂,⁶ Fe₂O₃⁷ and Nb₂O₅.⁸ As these oxides behave as good Lewis acids, the coated celluloses have been used in separation processes⁹ for enzyme immobilization,¹⁰ to prepare semi-permeable membranes¹¹ and to support electroactive chemical species for use as potentiometric sensors.¹²

The hybrid organic-inorganic material, Cel/Al₂O₃, is of particular interest. In this material aluminum oxide can be obtained in a highly dispersed form on the fiber surface with a good degree of adhesion.¹² In this material, the surface Al–OH groups can react easily with reagents containing terminal Si–OH groups forming a very stable Al–O–Si bonds.^{13,14}

This work reports the preparation and characterization of cellulose acetate-alumina, Cel/Al₂O₃, hybrid organic-inorganic material coated with N-propyl-1,4-diazabicyclo [2.2.2] chloride. The material obtained was furthermore applied in adsorption of MCl_n (M= Co(II), Fe(III) and Cu(II)) from ethanol solutions.

Experimental

Preparation of Cel/Al₂O₃. 10 g cellulose acetate (Aldrich: 39.7 wt% acetyl content; see the structure and numbering in Figure 1) was immersed in a solution containing a mixture of 37 g of acetone and 50 g of glacial acetic acid. The mixture was stirred for 8 h until resulting in a viscous homogeneous syrup (solution A). In a separated

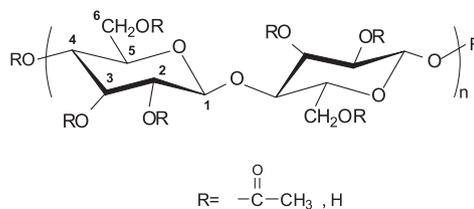


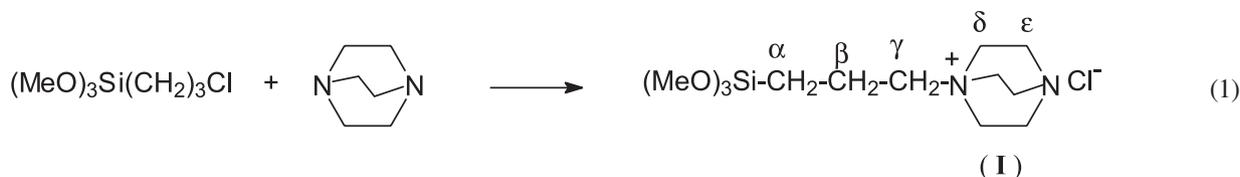
Figure 1. Cellulose acetate.

flask, 7 g of aluminum isopropoxyde (Aldrich) was dissolved in a smallest possible volume of trifluoroacetic acid (about 1 mL) and then added to solution A. The content of solution A was slowly added, under vigorous stirring, in distilled water (about 2 L) whose pH was previously adjusted to around 10 with ammonium hydroxide. The fibers of the material obtained were separated from the solution by filtration and washed with distilled water until the effluent solution achieved pH 7. The fiber was washed with dry ethanol and the residual solvent pumped off in a vacuum line at pressure about 10⁻³ torr. The material obtained is hereafter designated as Cel/Al₂O₃.

Modification of Cel/Al₂O₃. according to the procedure previously described by us^{15,16} and slightly modified in the present work, about 6 g of pure 1,4-diazabicyclo[2.2.2]octane was dissolved in 50 mL of dry toluene and 10 mL of 3-chloropropyltrimethoxysilane (Aldrich) was added. The solution was stirred at 383 K under dry nitrogen atmosphere for 2 h. The solvent was pumped off under vacuum and the remaining oily product was dissolved in 50 mL of ethanol and 20 g of Cel/Al₂O₃ was added and the solvent was slowly evaporated at 353 K.

The reactions involved in the preparation procedures can be represented by the equations 1 and 2, where $\sigma = \text{Cel}/\equiv\text{AlOH}$ and $\equiv\text{AlOH}$ is the aluminol groups of alumina dispersed on the cellulose acetate surface.

Chemical analyses. The amount of alumina incorporated into the Cel/Al₂O₃ matrix was determined by igniting 0.2 g of the material at 1173 K for 3h. The residue was weighed as Al₂O₃. The amount of diamine bonded to propyl group (II) was determined by titrating the ionized chloride with the standard AgNO₃ 0.01 mol L⁻¹ solution by the potentiometric method.



Infrared spectra

The infrared spectra of the materials for samples (2 wt%) in KBr pellets were obtained between 4000 and 400 cm^{-1} on a Bomem FTIR MB series spectrophotometer.

Adsorption isotherms

The adsorption isotherms of FeCl_3 , CoCl_2 and CuCl_2 from the ethanol solutions were measured at 298.0 ± 0.5 K. The precise weights of the material (approximately 0.1 g) were immersed in 50 mL of MCl $_n$ ethanol solutions of variable concentrations. The mixtures were stirred for 3h and the amounts of the metal halides in solutions after sorption were determined by complexometric titration using the standard edta 0.01 mol L^{-1} solution. The amounts of the adsorbed metals, N_f (in mol g^{-1}), were determined by applying the equation $N_f = (N_a - N_s)/m$, where N_a is the initial amount of metal in solution phase (mole), N_s is the amount of metal in solution after sorption (mole) and m is the mass of the adsorbent (g).

The ^{13}C NMR spectra of the solid products were obtained by CP MAS technique on a Bruker AC 300P spectrometer. The following conditions were used: pulses sequences with contact time of 1 ms with 2s interval and acquisition time of 60 ms. Tetramethylsilane was used as reference to calibrate the chemical shift.

Results and Discussion

Characterization of the material

The concentration of alumina incorporated in $\text{Cel}/\text{Al}_2\text{O}_3$ was 13.8 wt%. The degree of attached organic molecule in (II), determined by N elemental analysis, was $N = 4.1$ wt% or 1.46 mmol g^{-1} (quantity of diamine per gram of the material). Titration of the ionized chloride by the standard AgNO_3 solution gave the estimate 1.32 mmol g^{-1} .

Figure 2 shows the infrared spectra of (I) (Figure 2a), (II) (Figure 2c) and cellulose acetate (Figure 2b).

The marked peak at 1100 cm^{-1} (Figure 2a) is assigned to the asymmetric Si–O stretching mode.^{17,18} This band peak is shifted to 1070 cm^{-1} (Figure 2c) after the coating reaction with (I). This shift is presumably due to the Si–O–Al bond formation indicating that compound (I) is covalently bonded to the $\text{Cel}/\text{Al}_2\text{O}_3$ surface. The spectrum of cellulose acetate is also shown (Figure 2b) for comparison. As the interaction of (I) with $\text{Cel}/\text{Al}_2\text{O}_3$ involves only the free $\equiv\text{AlOH}$ groups on the cellulose modified surface, vibrational bands due to the cellulose matrix are not affected in (II).

Figure 3 shows the ^{13}C NMR spectra of (I), (II) and cellulose acetate. In Table 1 the chemical shift values and the respective assignments are summarized. The peaks at δ 53 and 45, assigned to the diamine C^δ and C^ϵ respectively for (I) and (II), do not show any significant change. This indicates that free nitrogens in the diamine groups bonded to the $\text{Cel}/\text{Al}_2\text{O}_3$ matrix do not interact with the polar unreacted $\equiv\text{AlOH}$ groups. Usually basic nitrogen atoms, included in amines or diamines attached to $\text{Cel}/\text{Al}_2\text{O}_3$

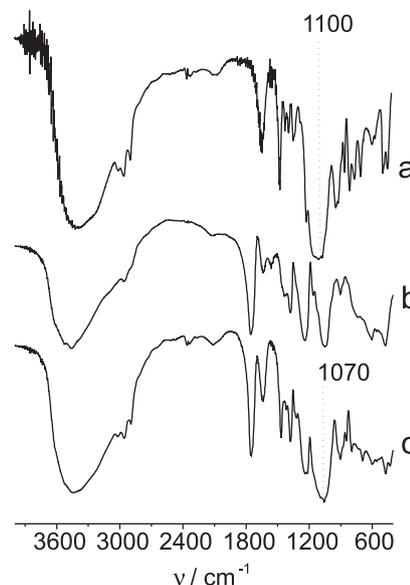


Figure 2. Infrared spectra of: a = (I), b = cellulose acetate and c = (II).

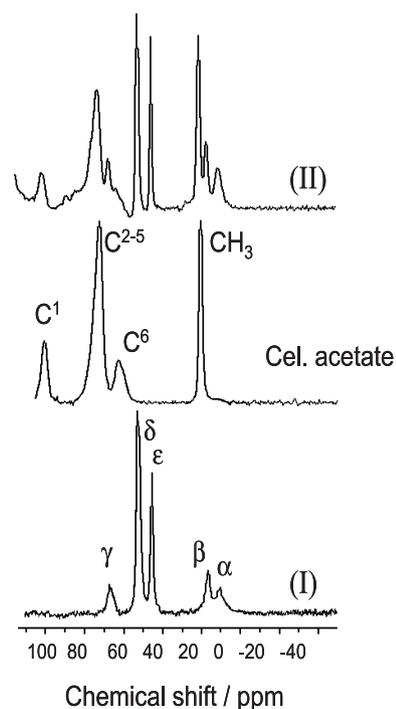


Figure 3. ^{13}C NMR spectra of (I), (II) and cellulose acetate.

Table 1. ^{13}C NMR chemical shifts for (I), (II) and cellulose acetate and the corresponding assignments

| Materials | δ / ppm | Assignments |
|--------------------------------|----------------|-----------------------------------------------------------------------|
| (I) ^a | 11 | C ^{α} |
| | 17 | C ^{β} |
| | 67 | C ^{γ} |
| | 53,45 | C ^{δ} , C ^{ϵ} |
| Cellulose acetate ^b | 102, 67 | C ¹ , C ⁶ |
| | 73 | C ²⁻⁵ |
| | 21 | CH ₃ |
| (II) ^a | 11 | C ^{α} |
| | 17 | C ^{β} |
| | 21 | CH ₃ |
| | 67 | C ^{γ} , C ⁶ |
| | 53, 45 | C ^{δ} , C ^{ϵ} |
| | 102 | C ¹ |

^aref. 6; ^bref. 19.

matrices, interact strongly with the polar surface groups.²⁰ In the present case as one nitrogen is positively charged, the opposite nitrogen is expected to have the basicity considerably lowered.

Adsorption isotherms and constants of the adsorption equilibria

Figures 2-4 show the adsorption isotherms for FeCl_3 , CoCl_2 and CuCl_2 from the ethanol solution on material (II) at 298 K.

The paramagnetic and spectroscopic measurements²¹ gave no evidence that the free nitrogen atom in fixed diamine interacts directly with the metal atoms and the species in which the nitrogen atom are included into the inner coordination sphere are formed. On the contrary, it was shown that metal chlorides may be immobilized on the surface in the form of the anionic chlorocomplexes that are electrostatically attracted by the positively charged surface groups²². Hence, it was supposed that the adsorption of FeCl_3 is due to the reaction



where the solid surface (II) is abbreviated as $\sigma\text{-L}^+\text{Cl}^-$, while in the case of CoCl_2 and CuCl_2 the surface species $(\sigma\text{-L}^+)_2 [\text{MCl}_4]^{2-}$ (M = Co or Cu) are formed.

The numerical analysis of the adsorption isotherms makes it possible both to test the hypothesis on the mechanism of adsorption and to characterize the adsorption equilibria quantitatively. As the methodology of the simulation and the computational approach were recently described elsewhere,^{23,24} only a few comments will be made here.

In the simplest case the adsorption process may be represented as follows:



where S denotes the neutral metal chloride, $\overline{\text{Q}}$ is the adsorption center and $\overline{\text{SQ}}$ is the surface complex, β is the constant of the adsorption equilibrium. According to this scheme any species (particularly, Cl^-) do not pass into solution. If both the effects of the surface energetic heterogeneity and the neighboring interactions are absent, the adsorption equilibrium (equation 4) is described by the Langmuir equation:

$$N_f \equiv [\overline{\text{SQ}}] = t_Q \times \frac{\beta \cdot [\text{S}]}{1 + \beta \cdot [\text{S}]} \quad (5)$$

where $N_f \equiv [\overline{\text{SQ}}]$ is the specific concentration of the adsorbed species S, mol g⁻¹; t_Q is the specific concentration of the sorption centers, mol g⁻¹; [S] is the equilibrium concentration of S in solution, mol L⁻¹. Equation 5 is easily transformed into the linear one:²⁵

$$\frac{1}{D} = \frac{[\text{S}]}{N_f} = \frac{1}{\beta \cdot t_Q} + \frac{1}{t_Q} \times [\text{S}] \quad (6)$$

where $D = N_f / [\text{S}]$ is the distribution ratio (L g⁻¹). The linear character of the plot (1/D) vs. [S] proves visually the validity of the assumptions made.

In order to have a quantitative description of the adsorption at the solid-solution interface, fitting of the isotherms by the Langmuir equation (method I) and fitting of the inverse distribution coefficients (method II) were used to obtain the calculated adsorption capacities t_Q and the equilibrium constants β .

In method I, the unknown parameters, t_Q and β , were found by minimization of the criterion:

$$U = \sum_{i=1}^j (N_{f,\text{exp}}^2 - N_{f,\text{calc}}^2)^2 \quad j = \text{number of experimental points} \quad (7)$$

where $N_{f,\text{calc}} = t_Q \frac{\beta [\text{MCl}_n]}{1 + \beta [\text{MCl}_n]}$. As usually, the adequacy of the models was tested with the use of the chi-square criterion.^{23,24}

In method II, the linear least-squares method was applied to equation 6, and the target parameters t_Q and β were found from the calculated regression coefficients.

The calculations have demonstrated that the model tested fits the experimental adsorption isotherm in error of 2.5-5% that corresponds to the level of the random errors. In Figures 4a, 5 and 6 the solid lines present the adsorption

isotherms simulated on the base of results obtained by method I. Figure 4b shows the linearized Langmuir equation, by applying equation 6, and illustrates the FeCl₃ adsorption, for which the correlation coefficient $r = 0.99$ was obtained. For CoCl₂ and CuCl₂ the correlation coefficients were 0.99 and 0.98 respectively and thus the graphics presenting the linear plots are not shown.

The numerical values of the target parameters t_Q and β , obtained by the both computational methods, have coincided with each other in the limits of errors of their determination that also corroborates the validity of the approach.

While fixed at the surface, CoCl₂ and CuCl₂ are transformed into the anions [CoCl₄]²⁻ and [CuCl₄]²⁻ each of them binds two monocharged diamine entities. It may seem that in such case the adsorption process should be represented by the scheme



But this contradicts to the model of equilibrium expressed by equation 4, where one sorption center binds one metal chloride entity. The contradiction is easily overcome with the help of the model of fixed polydentate centers.²⁶ According to it, the surface of the material is considered as the assemblage of centers, and each center

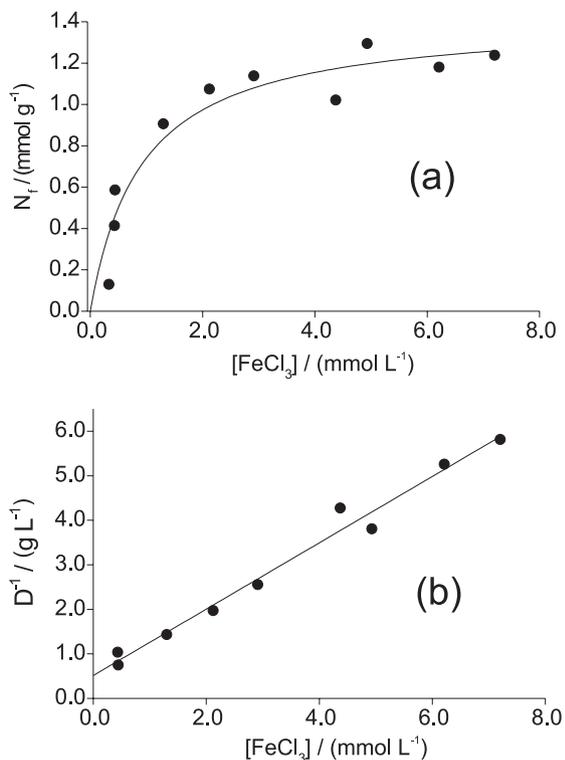
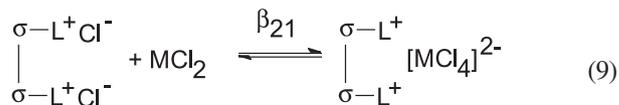


Figure 4. (a) The adsorption Isotherm of FeCl₃ from the ethanol solution at 298 K; (b) The corresponding fit by the linearized Langmuir equation.

contains several attached functional groups. Hence, the adsorption of MCl₂ (M = Co or Cu) may be described by the model of fixed bidentate centers in the following way:



where the first index at β points to the size of the polydentate center while the second one corresponds to the number of metal chloride entities bound by each center. Thus, the t_Q values, calculated from the CoCl₂ and CuCl₂ adsorption isotherms, correspond to pairs of the attached nitrogen containing groups rather than single ones.

The results of calculations are summarized in Table 2. For the FeCl₃ adsorption t_Q denotes the specific concentration of the adsorption centers $\sigma-L^+Cl^-$ and the equilibrium constant is β_{11} . For the CoCl₂ and CuCl₂ adsorption the specific concentrations of the active pairs of the attached groups, $\{\sigma-L^+Cl^-\}_2$, are presented, while the equilibrium constants are β_{21} .

The calculated t_Q values show that for FeCl₃ this value is much higher than those calculated for CoCl₂ and CuCl₂. This trend is consistent with reaction represented by

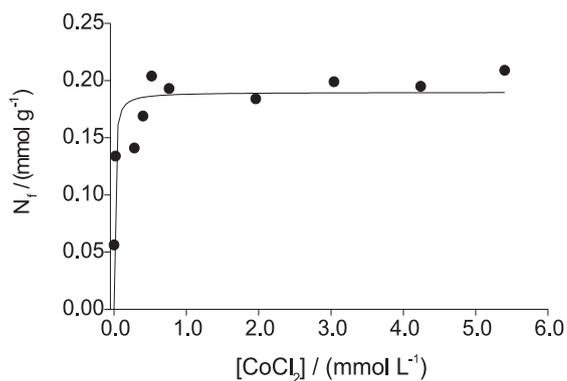


Figure 5. The adsorption Isotherm of CoCl₂ from the ethanol solution at 298 K.

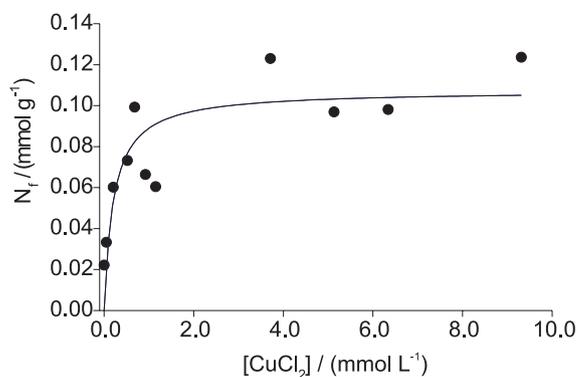


Figure 6. The adsorption Isotherm of CuCl₂ from the ethanol solution at 298 K.

Table 2. The characteristics of the FeCl₃, CoCl₂ and CuCl₂ adsorption equilibria at 298 K. The values in parenthesis are the standard deviations of parameters

| Metal halides | t_Q^a | $\log \beta^b$ |
|-------------------|---------------|----------------|
| FeCl ₃ | 1.42 (0.11) | 3.14 (0.14) |
| CoCl ₂ | 0.20 (0.01) | 4.08 (0.25) |
| CuCl ₂ | 0.115 (0.005) | 3.3 (0.3) |

^a t_Q /mmol g⁻¹; ^b β / L mol⁻¹.

equations 3 and 9 where the species formed on the substrate surface are FeCl₄⁻, CoCl₄²⁻ and CuCl₄²⁻. The values of equilibrium constants are not so different being slightly higher for adsorption of CoCl₂. The adsorption capacities t_Q are also dependent on the stability constants of each species [MCl_{n+m}]^{m-} since more stable is the anionic complex more strongly it will bind to the surface by electrostatic nature bonding. Unfortunately, data on stability constants of these species in ethanol solutions are scarce and not available for using in the present case.

Conclusions

The new hybrid material cellulose/Al₂O₃ coated with N-propyl-1,4 diazabicyclo [2.2.2] octane chloride group is very stable and show high adsorption capacity in adsorbing MCl_n from ethanol solution, presenting the following decreasing order: FeCl₃ >> CoCl₂ > CuCl₂. The results obtained are consistent with diffusion of MCl_n as neutral species into the substrate/solution interface and formation of the [MCl_{n+m}]^{m-} anionic complex bound on the surface by electrostatic interaction. There are no evidences that any covalent interaction between the free nitrogen of the diamine with the metal halide is occurring.

Acknowledgments

Y.G. is indebted to FAPESP for financial support (grant N^o 00/11103-5) and for an undergraduate student fellowship for G.S. Financial support from CNPq/Pronex is also acknowledged. Y.K. is grateful to the Ukrainian Ministry of Education and Science and V.N. Karazin Kharkov National University for the financial support through Project 15-15-00 "Quantitative characteristics of complexation processes in heterogeneous and micro-heterogeneous media".

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Received: August 21, 2003

Published on the web: February 17, 2005