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Some thermodynamic data about amino chrysotile derivatives with nickel and cobalt cation interactions in aqueous solution

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Abstract

Two silylating agents yielded aminopropyl and propylethylenediamine chrysotile derivative fibers named CRI1 and CRI2. The amount of organic groups of 1.20 and 2.87 mmol per gram of the fibers, were anchored on surface, respectively. The interactions between the amino groups attached to organic chains of these modified chrysotiles and divalent nickel or cobalt cations in aqueous solution were followed through calorimetric titrations. The thermal effect obtained from the interactive process was subtracted the respective thermal effect of dilution, which net value was adjusted to a modified Langmuir equation. The adsorption capacities were more pronounced for CRI1 and both processes were associated with complexes formation and the calorimetric data showed two defined steps for this fiber. The enthalpy of interaction was calculated to give the following values for CRI2: -78.61 ± 0.36 and -179.18 ± 6.44 kJ mol^{-1} for nickel and cobalt. Exothermic data for CRI1 contrasted to the previous values, giving 35.53 ± 0.50 kJ mol^{-1} for nickel and 25.73 ± 0.64 kJ mol^{-1} for cobalt, which value is related to two individual contributions of 13.94 ± 0.42 and 11.79 ± 0.22 kJ mol^{-1}. The negative Gibbs free energy values indicated a more favorable reaction for CRI2. A linear correlation was obtained between Gibbs free energy and Pearson's parameters related to hard–soft properties, suggesting that these processes can be adjusted to acidic–basic interactions. By including copper, the sequence of acidic hardness was $Co^{2+} > Ni^{2+} > Cu^{2+}$, which is the same order of free energy values found for both investigated systems. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chemically modified surfaces obtained through silylating reactions are object of many studies on chemistry of materials [1–10]. In this process, organofunctional silanes of general formula $X_3Si–Y$, where Y is the organofunctional moiety and X is normally a hydrolyzable group such as alkoxy, which favors the covalent bond formation on surface, due to the reactivity of OH groups disposed on to the inorganic surface. The proposed mechanism involves two steps: (i) the conversion of X groups to reactive silanol groups formed during the hydrolysis and (ii) the direct interaction of the formed silanol groups with the hydroxyl groups on inorganic surface [11].

Many matrices such as silica gel, phyllosilicate and oxides are favorable for such kind of reactions [1–10]. Thus, the modified surfaces show a set of new properties, which differ considerably from the precursor

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matrix. From the chemical point of view, the possibility of anchoring chelating agents contain nitrogen atom as basic centers improved the capacities of adsorption associated with the use of these matrices for extracting cations from aqueous and non-aqueous solutions [12–16].

The present investigation deals with the amino groups covalently bonded to an organic chain attached to chrysotile surface. This inorganic support is a hydrated magnesium silicate which backbone of the inorganic structure consists of a tetrahedral silica layer overlapped by magnesium hydroxide layers to give free Mg–OH groups on external surface [17]. After chemical modification through the use of distinct silylating agents, the original properties of this phyllosilicate have been changed. On the other hand, the natural chrysotile fibers have available on its surface the free reactive Mg–OH groups, which ability in interacting is demonstrated as molecular adsorption for enzymes [18], cationic surfactants [19], metal ions [20] or pigments [21].

The aim of this publication is focused on the chelate action developed by two distinct amino chrysotile derivatives with nickel and cobalt from diluted aqueous solution. The coordination ability of these ligands can be followed using calorimetric measurements and the proposed cation–surface interaction can also be better understood from the thermochemical point of view.

2. Experimental

2.1. Chemicals

Chrysotile samples of 7 ml with fiber length less than 2.0 mm were supplied by the SAMA'S mine, Uruaçu, Goiás, Brazil, which percentages in weight for SiO_2, Al_2O_3, MgO, Fe_2O_3 and H_2O were determined as 42.5, 1.12, 38.2, 4.05 and 14.13%, respectively.

The silylating agents 3-aminopropyltrimethoxisilane $H_2N(CH_2)_3Si(OCH_3)_3$ (Aldrich) and (*N*-[3-(trimethoxysilyl)propyl]ethylenediamine $H_2N(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$ (Fluka), magnesium chloride hexahydrate (Fluka), ethanol and sodium hydroxide (Merck) are all reagent grades. Hydrated divalent copper nitrate (Merk) was used in all adsorption processes. With exception of ethanol, all other chemical grade reagents were not further purified. Double distilled water was used in all experimental procedures.

2.2. Synthesis of modified fibers

Samples of chrysotile were initially washed under a strong water flow on a sieve of 0.0062 mm for 10 min. After then, the material was dried for 12 h at 393 K. The process of activation was performed by heating the samples for 2 days at 393 K in vacuum. The synthetic procedure consisted in reacting 5.0 g of activated asbestos with 5.0 cm^3 of 3-aminopropyltrimethoxysilane or *N*-[3-(trimethoxysilyl)propyl]ethylenediamine in xylene. The suspension was refluxed under an atmosphere of nitrogen for 5 days at 353 K with mechanical stirred. After cooling, the mixture of fibers was filtered, washed with a large volume of ethanol and dried in vacuum for 8 h at 353 K, to yield the matrices named as CRI1 or CRI2, relating to anchored fibers containing one or two amino centers, respectively. The degree of functionalization was determined by the amount of nitrogen content as determined by the Kjeldahl's method.

2.3. Characterization

Powder XRD patterns were obtained with nickel-filtered Cu Kα radiation on a Shimadzu model XD3A diffractometer (30/20 kV/mA).

Infrared spectra were obtained by using a Perkin-Elmer model 1600 FTIR spectrophotometer in KBr pressed pellet technique, in the 4000–400 cm^{-1} with the resolution of cm^{-1}.

Thermogravimetric curves were performed by using a DuPont model 1090 B apparatus coupled with a thermobalance 951 heated from room temperature to 1273 K at a heating rate of 0.16 K s^{-1} in argon atmosphere flux of 1.67 cm^3 s^{-1}, with samples varying in weight from 15.0 to 30.0 mg.

Carbon, nitrogen and hydrogen contents were determined by using a Perkin-Elmer microelemental analyzer.

Absorption atomic measurements were performed on a Perkin-Elmer instrument, model 5100, to determine the amount of cation supernatant after the adsorption process.

2.4. Adsorption of cations

The adsorption processes were followed batchwise in aqueous solution for cobalt and nickel (II) nitrates at 298 ± 1 K. For these adsorption measurements, samples of about 90 mg of fibers were suspended in 15.0 cm^3 of aqueous solution containing variable amounts of each cation. The initial concentration of the cations varied in the 2.0×10^{-5}–2.0×10^{-3} mol dm^{-3} range. The system was maintained in a thermostat bath under stirring at 298 ± 1 K for 3 h. After equilibrium established the suspension was centrifuged to separate the fibers and aliquots of the supernatant were carefully pipetted. The amount of metallic cations in solution was determined by atomic absorption. For each determination the reproducibility was checked by at least one duplicate experiment. The fixed number of moles of cation N_f per gram of solid was determined by equation $N_f = (N_i - N_s)/m$, where N_i is the initial amount of cation added, N_s the number moles in the supernatant and m the amount of fiber in grams used in each experiment.

2.5. Calorimetry

The calorimetric titrations were followed on a differential isothermic LKB 2277 microcalorimetric system previously described [22,23]. For each titration, a sample of approximately 90 mg was suspended in 15.0 cm^3 of double distilled water in a glass ampoule and was vigorously stirred in a thermostat bath at 298.15 ± 0.02 K. After equilibrium, aliquots of the solution of metallic cation were added through a microsyringe, coupled to calorimetric vessel. For each added increment of solution, the thermal effect ($\Delta_{tit}Q$) was recorded until the saturation of the surface is reached, which is indicated by a constant thermal effect recorded. However, the same procedure was used to monitor the thermal effect of the titration of the cation solution in water ($\Delta_{dil}Q$) without the solid and also the water to fiber suspension. The thermal effect of hydration of the modified fibers gave a null value. By combining those two thermal effect values, the resulting integral thermal effect ($\sum \Delta_r Q$) can be determined by the expression $\sum \Delta_r Q = \sum \Delta_{tit} Q - \sum \Delta_{dil} Q$, as illustrating by collecting the calorimetric titration data of nickel nitrate in aqueous solution on CRI1 as shown in Fig. 1.

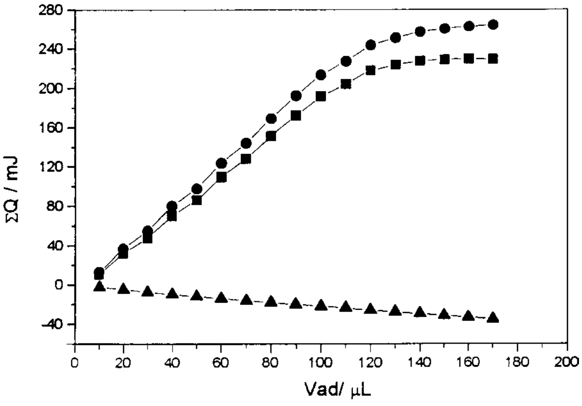

Fig. 1. Calorimetric titration of a suspension of 0.01813 g of CRI1 in 15.0 cm^3 of water with 0.70 mol dm^{-3} of $Ni(NO)_3$ solution in the same solvent at 298.15 ± 0.02 K. The experimental points represent the sum of the thermal effects of the cation titration $\sum Q_{tit}$ (–●–), cation dilution $\sum Q_{dil}$ (–▲–) and the net thermal effect of interaction $\sum Q_{int}$ (–■–). $\sum Q$ and V_{ad} values are the sum of detected thermal effect and total injected volume of salt solution, respectively.

The change in enthalpy associated with cation–fiber interactions ($\Delta_{int}h$) can be obtained by adjusting the data of the adsorption to the batch process performed in identical conditions, whose results were conformed to a modified Langmuir equation.

2.6. Thermochemical data treatment

The interactive processes were fitted to a modified Langmuir Eq. (1):

$$\frac{C_s}{N_f} = \frac{C_s}{N_s} + \frac{1}{(N_s \times b)} \qquad (1)$$

where C_s is the remaining cation concentration (mol dm^{-3}) in solution after equilibrium, N_f the amount of cation adsorbed (mol g^{-1}), N_s the maximum amount of adsorbed cation per gram of adsorbent matrix (mol g^{-1}), which depends on the number adsorption sites and b a parameter associated with the equilibrium constant for the reaction. N_s and b values can be estimated from the coefficients after linearization of the isotherm [24]. The agreement of both methods reflected in very close N_s values obtained from batch and calorimetric techniques.

The enthalpy of interaction $\Delta_{int}h$ was obtained by an expression derived from the modified

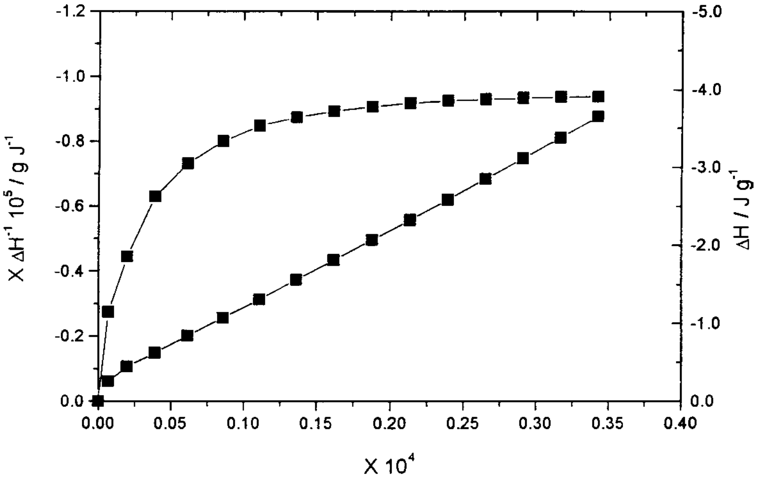

Fig. 2. Isotherm for the integral enthalpy of adsorption ($\Delta_r h$) versus molar fraction (X) obtained from a calorimetric titration of a suspension of CRI2 in 15.0 cm^3 of water, with 0.70 mol dm^{-3} of Ni(NO$_3$)$_2$ solution in the same solvent at 298.15 ± 0.02 K. The straight line is the linearized form of the isotherm.

Langmuir Eq. (2):

$$\frac{X}{\Delta_r h} = \frac{1}{(K-1)\,\Delta_{\text{int}} h} + \frac{X}{\Delta_{\text{int}} h} \qquad (2)$$

where X is the sum of the molar fractions of the remaining metallic cation in solution after interaction, $\Delta_r h$ the integral enthalpy that is obtained by the quotient between $\sum Q_r$ per mass of the fiber and K a constant of proportionality that includes the equilibrium constant. Here, $X/\Delta_r h$ versus X plot gave the angular and linear coefficients, which determine $\Delta_{\text{int}} h$ and K, respectively, as is illustrated in Fig. 2. The molar enthalpy of interaction process can be calculated by expression $\Delta H^0 = \Delta_{\text{int}} h / N_f$. K value is used to obtain the free Gibbs energy through the expression, $\Delta G = -RT \ln K$, and entropy value is calculated by means of the expression: $\Delta G = \Delta H - T\Delta S$.

3. Results and discussion

A remarkable feature associated with chrysotile fibers related with the intrinsic reactivity is its identical behavior as observed for other inorganic surfaces covered with hydroxyl groups. These specific groups are very sensible in the well-known interaction with silylating agents [5,6]. After fiber modification, the anchored molecules favor the characterization through elemental analysis, infrared and RMN spectroscopies, and XRD and thermogravimetric techniques. Thus, the present series of results, with the modified fibers are comparable to that collected earlier [25] and the results were similar for the presented modified fibers.

Both silanized chrysotiles showed interlayer spacing of 770 pm values, while the precursor sample presented the distance of 743 pm. The small difference in interlamellar space suggests that this immobilization occurred just on surface.

The elemental carbon, hydrogen and nitrogen data are listed in Table 1. From these values the presence of 1.20 and 2.87 mmol g^{-1} of anchored organic groups on surfaces was calculated. These high values of silylating agents immobilized are in agreement that an effective interactive process takes place.

The thermogravimetric measurements showed a total mass loss of 19.0 and 25.5% for CRI1 and CRI2, respectively, which degree differs from 13.5% value

Table 1
Percentages (%) of hydrogen, carbon, nitrogen and C/N ratio expected and (calculated) for chemically modified chrysotiles CRIX (X = 1, 2)

Fiber	H (%)	C (%)	N (%)	C/N
CRI1	1.85	5.705	1.68	3.38 (3.0)
CRI2	3.93	17.19	8.02	2.14 (2.5)

found for the original fiber. This sequence of values support the argument that the immobilization are effective and the silylating agents are covalently attached on surfaces, but not as physical adsorbed species.

The infrared spectrum of chrysotile presents bands at 3690 and 3650 cm^{-1} attributed to the stretching frequencies of the ended Mg–OH species bonded on surface. However, the first band is due to free hydroxyl groups and the last one is assigned to the same groups located inside on the structure, as expected for the arrangement of the inorganic layers of this phyllosilicate.

The molar ratio between internal and external OH groups was established as 3:1, but the internal ones can suffer condensation on heating, causing the disappearance at temperatures above 833 K [26–28]. Hence, these groups are of low concentration and not easily accessible to chemical interaction with molecules of this diversity of reagents used for anchoring process. A set of three other important bands appeared at 1075, 1015 and 950 cm^{-1}, which can be attributed to (Si–O–Si) vibration modes [26–28].

For CRI1 and CRI2 matrices other new bands are added to those previous mentioned at 2930 cm^{-1}, assigned to the aliphatic C–H stretching frequency mode [29]. Again, in these spectra the same set of three bands associated with the Si–O–Si group appeared, but with different intensities.

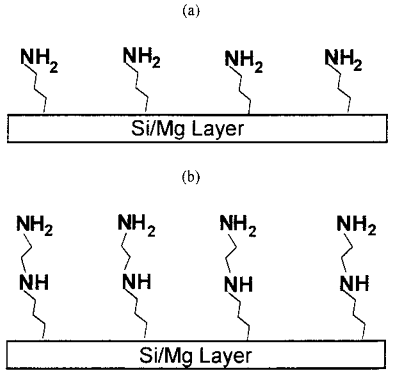

Fig. 3. Structure of modified fibers (a) CRI1 and (b) CRI2. The presence of silylating agent is limited only on surface.

The series of these determinations indicated the silylating coupling agents were covalently immobilized on surface of the precursor fibers and a proposed arrangement of these chains on structure are shown in Fig. 3.

The manifested adsorption properties of these anchored surfaces were illustrated by isotherms in Figs. 4 and 5. These interactions are associated with the formation of surface complex involving the amino groups and cations in aqueous solution, which evidenced the existence of acid–base reactions. The curves showed that the adsorptive capacities were

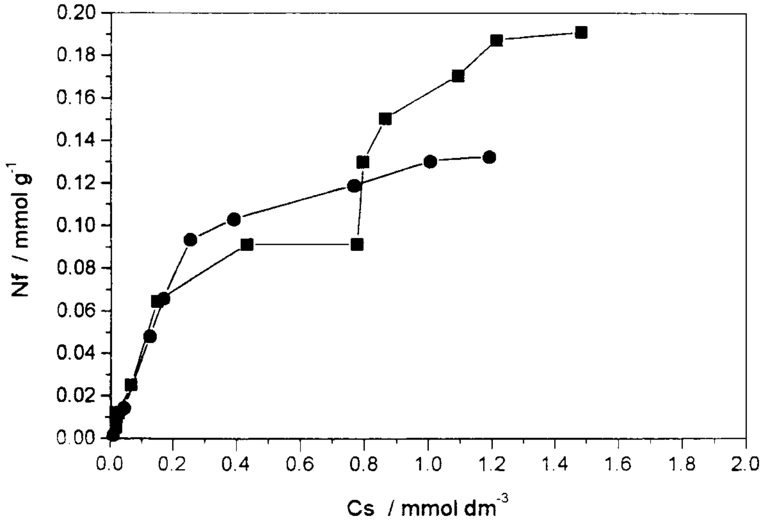

Fig. 4. Isotherms of interaction of cations Co^{2+} (–■–) and Ni^{2+} (–●–) on CRI1 surface.

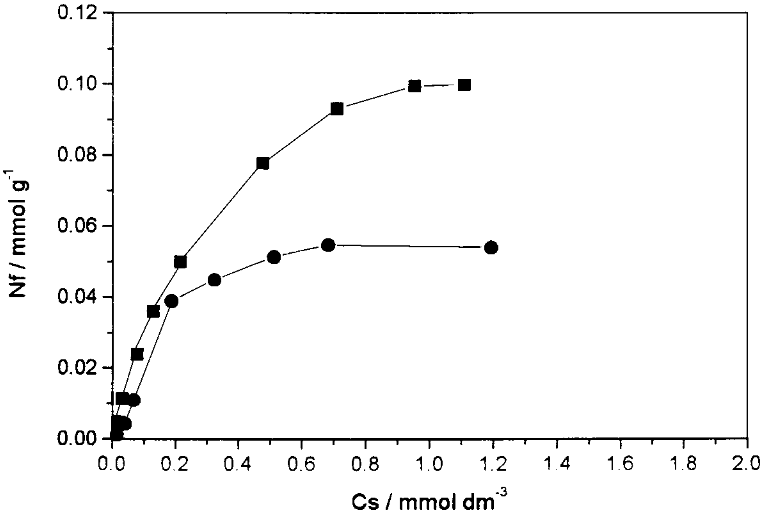

Fig. 5. Isotherms of interaction of cations Co^{2+} (–■–) and Ni^{2+} (–●–) on CRI2 surface.

more pronounced for CRI1 than CRI2 and the highest values for cobalt reflect the larger acidity of this cation. The experimental isotherms for aminopropyl fibers with cobalt nitrate interaction displayed in two steps, suggesting the presence of two classes of distinct basic sites on CRI1 surface.

The energetic of these interactive processes was obtained from calorimetric measurements as listed in Table 2. The values of enthalpy are endothermic for aminopropyl chrysotile, while exothermic values were obtained from diamino derivative fibers. The highest enthalpic values for CRI2 are in agreement with the presence of largest number of coordinate centers on this surface, which is favorable for the bidentate complex formation. Again the highest enthalpic value for cobalt reinforces its acidity.

The same behavior for this interactive process involving cobalt on aminopropyl chrysotile surface was detected by calorimetric isotherm, that confirmed the existence of two different adsorptive sites on these fibers, as illustrated by calorimetric curves showed in Fig. 6. The individual enthalpic contributions were 13.94 ± 0.42 and 11.78 ± 0.22 kJ mol^{-1}, respectively, for the first and second processes of cobalt adsorption, which gave the total enthalpic value of 25.72 ± 0.64 kJ mol^{-1}.

The variation in Gibbs free energy values suggested the existence of favorable processes. These values showed a linear correlation with Pearson's parameter as illustrated in Fig. 7. Therefore, a sequence of results for copper nitrate data was previously obtained for similar system [30].

The thermodynamic data reflect the adsorption mechanism for cations on modified fibers and the treatment of this interaction is adjusted to a typical acid–base model. The copper cation showed the lowest Pearson parameter value, which is in fact associated with its lowest hard acidic behavior [31]. These δ values decreased as increasing the softness of the correspondent cation in aqueous systems and for

Table 2
Thermodynamic data for metallic nitrates and modified chrysotile interaction at 298.15 ± 0.02 K

Fiber	M^{2+}	Δh_{int} (J g^{-1})	ΔH^0 (kJ mol^{-1})	$-\Delta G^0$ (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})
CRI1	Ni^{2+}	5.33 ± 0.15	35.53 ± 1.01	27.6 ± 0.1	212 ± 4
	Co^{2+}	41.44 ± 0.32	25.73 ± 0.64	29.7 ± 0.7	7 ± 4
CRI2	Ni^{2+}	-4.18 ± 0.02	-78.61 ± 0.36	32.4 ± 0.1	-155 ± 2
	Co^{2+}	-17.90 ± 0.67	-179.18 ± 6.44	32.8 ± 0.4	-491 ± 23

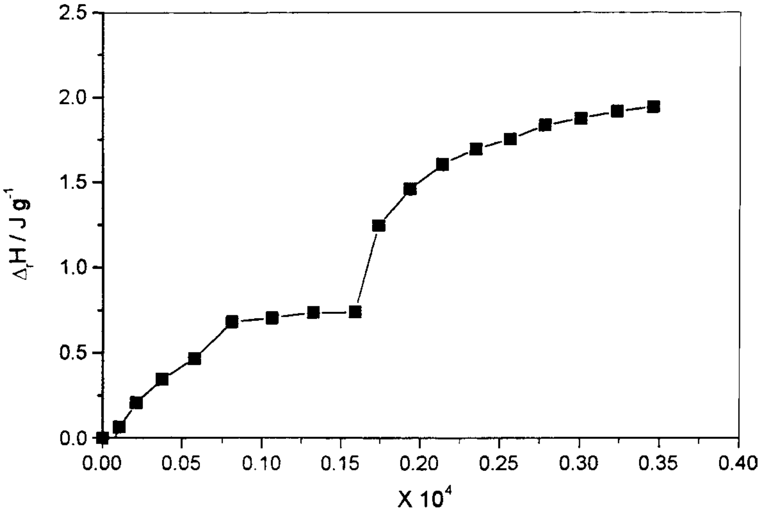

Fig. 6. Change in enthalpy against molar fraction plot of metallic cobalt in solution after interaction with CRI1 at 298.15 ± 0.02 K.

divalent copper, nickel and cobalt cations are: 0.104; 0.126 and 0.130, respectively. Thus, the hardness of the free acids follows the order $Co^{2+} > Ni^{2+} > Cu^{2+}$, suggesting that the adsorption process was more favorable in this sequence and also is in agreement with the collected free energy values for both modified fibers. This correlation indicated that the highest number of basic sites on fibers showed a more favorable process as observed for the highest exothermic values of free energy for CRI2 fiber.

The adsorption on CRI1 chrysotile reflects on a favorable entropic system, which is enthalpically unfavorable. On the other hand, an opposite behavior was observed for CRI2 surface, which maintained to final system an organized structure, revealing the favorability of the enthalpic contribution.

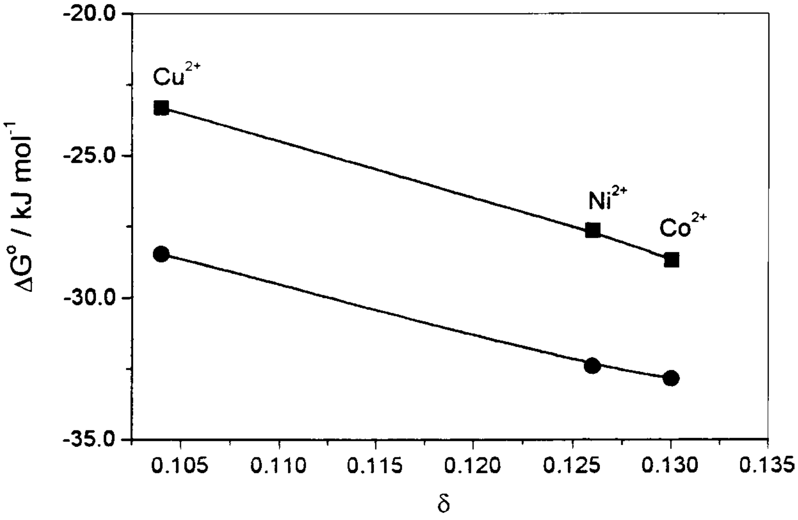

Fig. 7. Representation of the linear correlation between free energy change values and Pearson parameter δ for copper, nickel and cobalt cations with CRI1 (–■–) and CRI2 (–●–) modified chrysotiles.

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