КАЛОРИМЕТРИЧЕСКИЕ ДАННЫЕ ПО ФУНКЦИОНАЛИЗАЦИИ АРОМАТИЧЕСКИХ АМИНОВ В $NH_2[Zn_{2-x}Cu_xCo_x(PO_4)(HPO_4)$ (X≈0.6) НА ГРАНИЦЕ ТВЕРДОЕ/ЖИДКОСТЬ

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CALORIMETRIC DATA FOR AROMATIC AMINES FUNCTIONALIZATION INTO $NH_2[Zn_{2-x}Cu_xCo_x(PO_4)(HPO_4)$ (X≈0.6) AT THE SOLID/LIQUID INTERFACE

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The present investigation reports calorimetric determinations involving the functionalization of $NH_2[Zn_{2-x}Cu_xCo_x(PO_4)(HPO_4)]$ (x≈0.6) (CCZ-PH) with aromatic amines pyridine and ∝-, β-, and γ-picolines, by using the batch method in 1,2-dichloroethane, in order to study the energetic thermal effects of functionalization. The spontaneity of these systems, reflected in the negative Gibbs free energies and the favorable positive entropic values, agrees with the displacement of coordinated solvent molecules as the functionalization takes place. The functionalized matrices were named as CCZ-PH $_{PY}$, CCZ-PH $_{∝\text{-PIC}}$, CCZ-PH $_{β\text{-PIC}}$, and CCZ-PH $_{γ\text{-PIC}}$.

The functionalization reaction can be considered as an insertion of a mobile guest species into the host solid structure, while maintaining the framework structural characteristics and an acid/base reaction of the guest species takes place in the accessible empty holes of the inorganic structure. The maximum numbers of moles of the aromatic amines functionalized on CCZ-PH in 1,2-dichloroethane were obtained by supernatant titration as 2.18, 1.91, 1.79, and 1.59 mmol g^{-1} for CCZ-PH $_{PY}$, CCZ-PH $_{∝\text{-PIC}}$, CCZ-PH $_{β\text{-PIC}}$, and CCZ-PH $_{γ\text{-PIC}}$, respectively, showing a decrease in the sequence pyridine > ∝- > β- > γ-picolines (Table 1). This series does not correlate with the basicity as expressed by very similar pK_a values of 5.22, 6.12, 5.71, and 5.98 for pyridine, ∝-, β-, and γ-picolines, respectively. On the contrary, the methyl group position on aromatic ring influences the amount of amine inserted into the free gallery space of the inorganic matrix. The thermodynamic data related to amine functionalization into the free cavity of the CCZ-PH in 1,2-dichloroethane are listed in Table 1, resulting in an exothermic effect from the net interactive effects. The results showed that an increase in carbon number in the chain induces a corresponding enhancement in the exothermicity of the enthalpy of functionalization. For example, for pyridine and γ-picolines, the values of enthalpy of functionalization are -6.91 and -9.99 $kJmol^{-1}$, respectively, data which reflects a favorable energetic process of functionalization.

Table 1. Thermodynamic data for functionalization of aromatic amine molecules in 1,2-dichloroethane with original ammonium cobalt/copper-zinc phosphate at 298 ± 1 K.

Amine	N_f^{max} (mmol g^{-1})	$-\Delta_{mon}h$ (Jg^{-1})	$-\Delta_{ads}H$ ($kJmol^{-1}$)	$-\Delta_{mon}G$ ($kJmol^{-1}$)	$\Delta_{mon}S$ ($JK^{-1}mol^{-1}$)	r^2
Pyridine	2.18± 0.12	14.45± 0.13	6.91 ± 0.13	33.6 ± 0.1	90 ± 1	0.999
∝-Picoline	1.91± 0.12	14.89± 0.13	7.87± 0.15	35.8± 0.1	93± 1	0.999
β-Picoline	1.79± 0.15	15.27± 0.11	8.98± 0.13	37.9± 0.2	95± 1	0.999
γ-Picoline	1.59± 0.24	15.78± 0.11	9.99± 0.11	38.4± 0.1	97± 2	0.999

The Gibbs free energy values for all functionalizations were negative, indicating that the reactions are spontaneous in nature for all systems. Positive entropic values are also consistent with the arguments that the functionalization process is entropically favored. These values suggest a disruption of the molecules of the solvents originally bonded in the free cavity to the ammonium cobalt/copper-zinc phosphate, as the guest molecules are progressively functionalized. In addition, another contribution to the entropy comes from amine desolvation as the acidic centers on the ammonium cobalt/copper-zinc phosphate structure are saturated. Thus the entropic results can be related to the release of these solvent molecules to solution as the functionalization is in progress. Similar behavior was observed for other material in the functionalization process.

The organic content present in the functionalized materials was obtained by C, H, N, chemical analyses and results are listed in Table 2, with the integrity of the organic molecules being present in the lamellar structure confirmed from the calculated C/N ratios. Based on the analytical data for four nanocompounds, the density of these pendant organic molecules immobilized on the porous of the double hydroxide layer can be calculated. Thus, the precursor γ-picoline agent grafted onto ammonium cobalt/copper-zinc phosphate sample gave an amount of 6.345 mmol g^{-1}.

Table 2–Percentages of carbon (C), hydrogen (H), and nitrogen (N) for ammonium cobalt/copper-zinc phosphate functionalized with aromatic amines pyridine and ∝-, β-, and γ-picolines

Sample	C (mmol g^{-1})	H (mmol g^{-1})	N (mmol g^{-1})	C/N (calculated)	C/N (found)
CCZ-PH_{PY}	5.013	0.699	0.985	5.089	5
CCZ-$PH_{∝\text{-}PIC}$	5.944	0.739	0.979	6.069	6
CCZ-$PH_{β\text{-}PIC}$	6.035	0.859	0.985	6.136	6
CCZ-$PH_{γ\text{-}PIC}$	6.076	0.967	0.995	6.115	6

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