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Interaction of aliphatic diamines with vermiculite in aqueous solution

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Abstract

Vermiculite was reacted with aliphatic diamines (ethyl-, propyl-, butyl- and hexyldiamines). The products were characterized by elemental analysis, infrared spectroscopy and X-ray diffraction. The amounts of amines adsorbed were 0.89, 0.86, 0.79, and 0.68 mmol g^{-1}, respectively, for $NH_2(CH_2)_2NH_2$ where $n=2$, 3, 4, 6. The basal spacings of the intercalated vermiculites varied between 1.28 and 1.47 nm.

Keywords: Vermiculite; Diamines; Adsorption

1. Introduction

Many studies of synthesis of modified vermiculite have been published. Vermiculite-polymer nanocomposites for reinforcing purposes (Burnside et al., 1999; Tjong et al., 2002; Xu et al., 2003), vermiculite–alkylammonium for industrial applications (Jimenez de Haro et al., 1998) or pillared vermiculite as catalytic support has been investigated (Rey-Perez-Caballero and Poncelet, 2000; Nakatsuji et al., 2004).

The present investigation deals with the synthesis and characterization of hybrids derived from reaction of aliphatic diamines and vermiculite.

2. Experimental

2.1. Chemicals

The vermiculite samples (V) were obtained from the União Brasileira de Mineração Company from Santa Rita, state of Paraiba, Brazil. Chemical analyses of the sample were performed by AAS using a Perkin-Elmer 5100 Model instrument with an air–acetylene flame. The samples were digested in a mixture of HF–HCl. The CEC was measured using ammonium acetate buffered at pH 7.0 (Bache, 1976). The nitrogen content was determined on a Perkin-Elmer model 2400 analyzer.

Ethyl-, propyl-, butyl- and hexyldiamine (Aldrich) were used without treatment. Copper nitrate hexahydrate (Merck) was reagent grade and used without previous purification.

2.2. Reaction adsorption

A series of vermiculite samples of 50.0 mg was dispersed in 25.0 cm^3 of aqueous solutions, containing diamines of several concentrations, varying from zero to 0.010 mol

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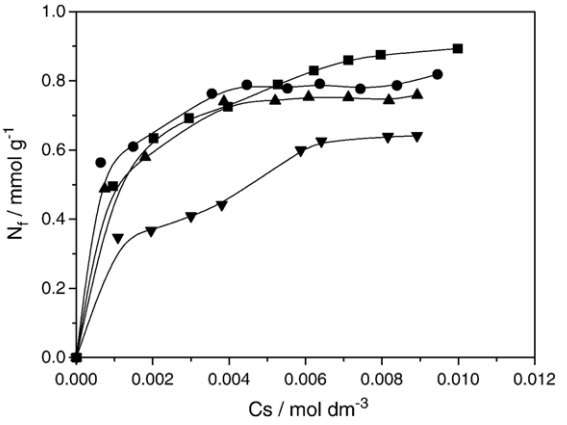

Fig. 1. Adsorption isotherms of vermiculite with ethyl- (■), propyl- (●), butyl- (▲), and hexyldiamine (▼) at 298±1 K.

dm^{-3}. The solutions were stirred for 48.0 h. This equilibrium time was previously determined at 298±1 K. The solid was separated by filtration. The amine concentrations were determined by acid–basic titration with HCl standard solution. The number of moles N_f amines adsorbed per mass m of the solid was determined by expression $N_f=(N_i-N_s)m^{-1}$, where N_i and N_s are the initial and final amount of the amine in solution, respectively. The intercalated vermiculites were characterized by infrared spectroscopy, X-ray diffraction and CHN elemental analysis.

The adsorption data were fitted to a modified Langmuir equation (Adamson, 1990):

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

where C_s is the equilibrium amine concentration (mol dm^{-3}), N_f is the amount of amine adsorbed (mol g^{-1}), N_s is the maximum amount of amine per gram of vermiculite (mol g^{-1}). The constant b depends on solvent properties such as density (d) and molecular mass defined by the expression $b=\frac{MK}{d}$. The two parameters N_s and b values can be estimated from coefficients after linearization of the isotherms.

2.3. Characterization

Carbon, hydrogen, and nitrogen contents were determined on a Perkin-Elmer model 2400 analyzer. At least two determinations were performed for each sample.

X-ray diffraction patterns were obtained by a nickel-filtered Cu$K\alpha$ radiation on a Shimadzu model XD3A diffractometric apparatus in the range $2\theta=1.5°$ to 70° and at a scan rate of 0.67° s^{-1}.

Infrared spectra between 4000 and 400 cm^{-1} were recorded on a Bomem MB-Series spectrophotometer. The FTIR spectra were obtained in transmittance mode on KBr pellets with 4 cm^{-1} of resolution and 35 accumulations.

The surface area was determined by the BET method in a Micrometrics Flowsorb II Apparatus.

3. Results and discussions

3.1. Original properties of vermiculite

The chemical composition of vermiculite in weight percentage was: SiO_2 (44.62); Al_2O_3 (9.18) Fe_2O_3 (5.46); CaO (0.78); MgO (20.44); Na_2O (0.11); K_2O (0.48) with loss of weight after heating at 1273 K (18.93). Based on the data, the structural formulae of the sample studied (calculated on the basis of $O_{20}(OH)_4$ per formula unit) were $Mg_{4.68}Ca_{0.128}Na_{0.032}K_{0.094}$-$Fe_{0.63}Al_{1.66}Si_{6.85}$ where Fe^{3+} is equal to total Fe on the basis of wet chemical analysis. The CEC was 135 meq/100 g and BET surface area was 16 m^2 g^{-1}.

3.2. Interaction isotherms

The reaction of ethyl-, propyl-, butyl- and hexyldiamine with vermiculite was followed by an acid–basic

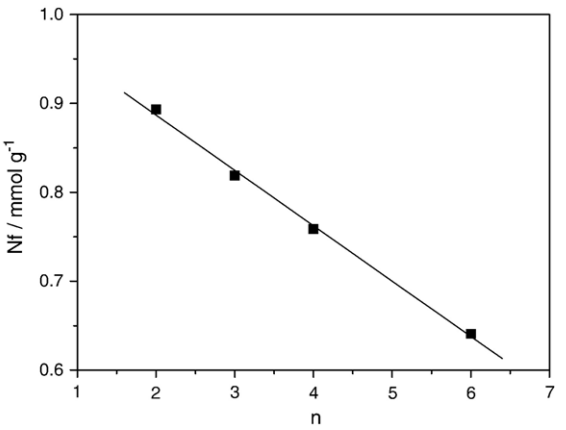

Fig. 2. Amines adsorbed, N_f, as a function of the number of carbons atoms n $NH_2(CH_2)_nNH_2$, from aqueous solutions at 298 K±1.

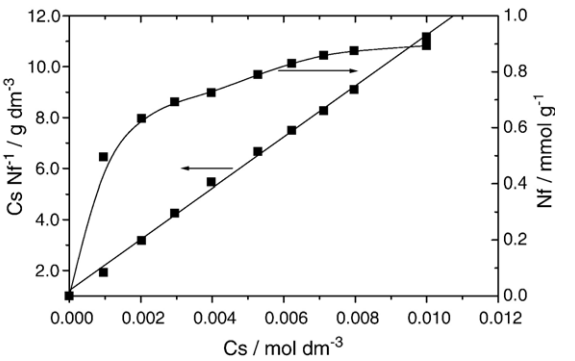

Fig. 3. Adsorption isotherm of vermiculite with ethyldiamine at 298 ±1 K and its linearized form.