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Vermiculite-aliphatic amine interactions at the solid/liquid interface: a thermodynamic approach

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Abstract Polar *n*-alkylmonoamines of general formula $H_3C(CH_2)_nNH_2$ ($n = 1, 3, 5$) interacted with layered silicate vermiculite at the solid/liquid interface. The maximum amount of amine intercalated (N_f) inside the interlamellar space were 0.62, 0.46, and 0.38 mmol g^{-1}, to give the following order of intercalation ethyl → butyl → hexylamines. The layered vermiculite solid was suspended in deionized water and calorimetrically titrated with this series of amines, to give favorable thermodynamic data, such as exothermic enthalpy, negative Gibbs free energy and positive entropy data.

Keywords Aliphatic amine · Calorimetry · Layered silicate · Vermiculite

Introduction

Clay mineral/organic molecule interactions are part of an advanced theme to be applied as a route to obtain new and technologically useful materials. For this purpose, phyllosilicate-organic reactions have been extensively investigated in order to generate a lot of information on different types of interactive mechanisms related to the multivariable reactions involving silicate layers, inorganic cations, water, and organic molecules [1]. Thus, a wide range of functionalities attached to organic compounds like amides [2, 3], amino acids [4], dyes [5, 6], amines [7, 8] and mercapto compounds [9] can interact with available functions on clay mineral surface, being montmorillonite the most explored clay mineral, mainly due to its swelling behavior.

Early investigations were carried out on adsorption of aliphatic amines on montmorillonite and vermiculite by employing cation exchanged process [10]. For this clay/basic molecule system, both magnitude of the layered charge and its homogeneity in distribution were taken into account, showing that the swelling behavior is closely related to the number of carbon atoms in the amine chain. Based on the reported data related, many investigations have focused attention on phyllosilicate/aliphatic amine interactions [10–13].

The great majority of these studies are normally applied by reacting desirable gaseous molecules through the solid surface and the change in properties are normally followed by the variation in the absorption spectra within the infrared region. On the other hand, a shortage of investigations is related on energy changes associated with these reactions at the solid/liquid interface. In an attempt to have more information on vermiculite/amine interactions, the present investigation deals with the thermal effect originating from the reactions between this natural clay and three aliphatic amines in aqueous solution. From this system the thermodynamic data were determined, after a complete characterization of the available layered precursor.

Experimental

Chemicals

Vermiculite was supplied by União Brasileira de Mineração Company from Santa Rita, state of Paraiba, Brazil.

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All reagents were of analytical grade. Ethyl-, butyl- and hexylamines (Aldrich) were used without further treatment.

Analytical procedures

Chemical analyses of the sample were performed by atomic absorption by using a Perkin-Elmer 5100 Model instrument with an air-acetylene flame, after the samples were digested in a mixture of HF-HCl solution. The cation exchange capacity (CEC) was determined by the ammonium acetate method [14]. The nitrogen content of the intercalated compounds was determined on a Perkin–Elmer model 2400 analyzer.

Potentiometric titration of amines was accompanied in a Gehaka model PG1800 pH apparatus with precision of ±0.01.

Adsorption isotherms

The isotherms of interactions were obtained through batchwise method, where 30 mg of vermiculite sample was suspended in 10.0 cm^3 of aqueous solutions, containing each amine at several concentrations, in the same condition used for calorimetric measurements, at 298 ± 1 K. The suspensions were mechanically stirred for 48 h that was previously established as optimal experimental condition to saturate the acidic centers on the support. The solid was separated by filtration and the free amine content in each suspension was measured by potentiometric titration. The number of moles of amines, N_f, in a mass m of the solid was evaluated by the expression $N_f = (N_i - N_s)\ m^{-1}$, where N_i and N_s are the initial and final amounts of the amine in solution, respectively.

The adsorption data were fitted to a Langmuir equation in a linearized form [15]:

$$\frac{C_s}{N_f} = \frac{C_s}{N_s^{\max}} + \frac{1}{(N_s^{\max} b)} \tag{1}$$

where C_s is the equilibrium amine concentration (mol dm^{-3}), N_f is the amount of amine adsorbed (mol g^{-1}), $N_s^{\max}$ is the maximum amount of amine per gram of vermiculite (mol g^{-1}). The two parameter $N_s^{\max}$ and b values can be estimated from coefficients after linearization of the isotherms.

Calorimetry

The thermal effects for all interactions were calorimetrically monitored by titrations using a differential isothermic LKB 2277 microcalorimetric system. For each titration, a sample of approximately 30 mg of the vermiculite was suspended in 2.0 cm^3 of double distilled water in a glass ampoule and was vigorously stirred in a thermostat bath at 298.15 ± 0.20 K. After equilibrium, aliquots of amine solutions were added through a microsyringe, coupled to calorimetric vessel. For each added increment of solution, the thermal effect, Q_{tit}, 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 amine solution in water, Q_{dil}. Another run consisted in suspending the solid vermiculite in the calorimetric solvent, which correspond to the thermal effect of the solid hydration that gave a null value. By combining those two thermal effect values, the resulting integral thermal effect, ΣQ_{r}, can be determined by $\Sigma Q_{\mathrm{r}} = \Sigma Q_{\mathrm{tit}} - \Sigma Q_{\mathrm{dil}}$. The enthalpy of interaction $\Delta_{\mathrm{int}}h$ was obtained by an expression derived from the modified Langmuir [15] Eq. 2

$$\frac{\sum X}{\Delta_i h} = \frac{1}{(K-1)\Delta_{\mathrm{int}} h} + \frac{\sum X}{\Delta_{\mathrm{int}} h} \tag{2}$$

where X is the sum of the molar fractions of the remaining amine in solution after interaction, $\Delta_{\mathrm{r}}h$ is the resulting integral enthalpy from the interactive process (J g^{-1}), which was calculated by dividing the thermal effect obtained from ΣQ_{r} by the mass of the solid (m) and K is a proportionality constant including the equilibrium constant. The plot of $X/\Sigma\Delta_{\mathrm{r}}h$ against X gave the angular and linear coefficients, which enabled the determination of $\Delta_{\mathrm{int}}h$ and K. The molar enthalpy of interaction process can be calculated by expression $\Delta H^0 = \Delta_{\mathrm{int}}h/N_f$, which N_f values where obtained, as described before. The K value was used to calculate the Gibbs free energy through the expression, $\Delta G^0 = -RT \ln K$, and entropy changes is calculated by means of the general expression: $\Delta G^0 = \Delta H^0 - T\Delta S^0$.

Results and discussion

The percentages in mass for the chemical composition of the pristine vermiculite gave the values: 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 mass loss of 18.93 % after heating at 1273 K. By considering the present data, the structural formulae of the sample studied, gave the following general composition $Al_{1.66}Si_{6.85}Mg_{4.68}Fe_{0.63}O_{20}(OH)_4Ca_{0.128}Na_{0.032}K_{0.094}$.

The reactions of ethyl-, butyl- and hexylamines with vermiculite were followed by an acid-base potentiometric titration as illustrated through the isotherms, as shown in Fig. 1.

The maximum amount intercalated were 0.62, 0.46, and 0.38 mmol g^{-1} for ethyl → butyl → hexylamine, respectively. These decreased values followed the increase in size of the alkyl chains of the amines. This same behavior in

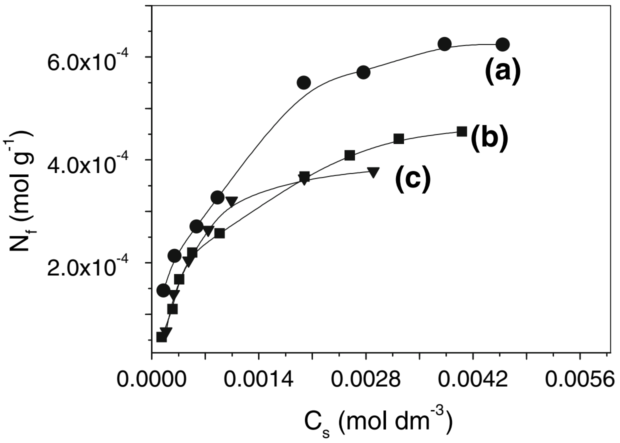

Fig. 1 Adsorption isotherms of (*a*) ethyl-, (*b*), butyl- and (*c*) hexylamines on vermiculite at 298 ± 1 K

decreasing values was also observed before for diamines with equivalent number of carbon atoms in the organic molecules, as given by the values 0.89, 0.76, and 0.64 mmol g^{-1} for ethyl-, butyl-, and hexyldiamines [16].

From the experimental data adjusted to the Langmuir model a reasonable coefficient of correlation was obtained for the maximum amount of amine adsorbed, as shown in Fig. 2.

N_f values obtained from batch method and N_s^{max} calculated values followed the same trend in behavior, which results are listed in Table 1.

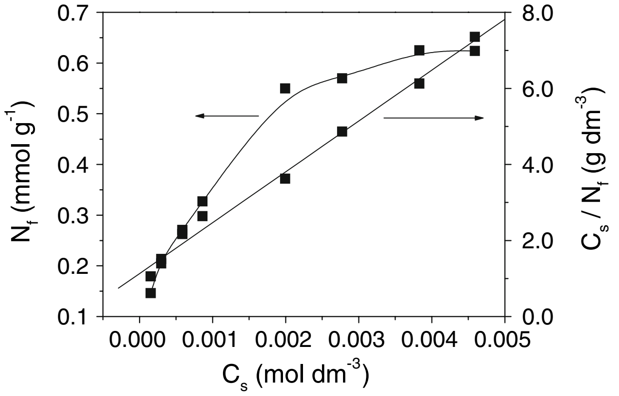

Fig. 2 Adsorption of ethylamine by vermiculite at 298 ± 1 K and its linearized form of isotherm

Table 1 Experimental values of N_f and the parameters N_s^{max}, b and R resulted from modified Langmuir equation applied for interaction of n-alkylamines and vermiculite in aqueous solution

$CH_3(CH_2)_nNH_2$	N_s^{max} (mmol g^{-1})	N_f (mmol g^{-1})	b (dm^3 mol^{-1})	R
$n = 1$	0.75	0.62	1183	0.9953
$n = 3$	0.57	0.46	958	0.9966
$n = 5$	0.46	0.38	1757	0.9973

Based on this observed result, it is suggested that the orientation of organic chains inside the interlamellar space is a preponderant effect in this type of process. On the other hand, this same behavior was previously observed for other

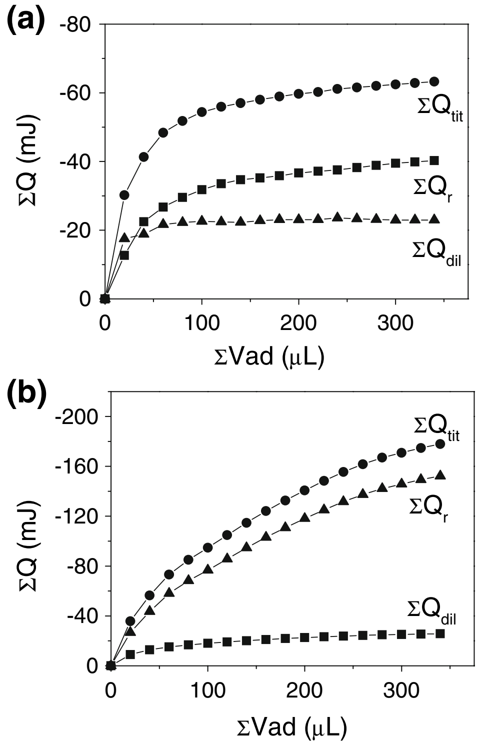

Fig. 3 Calorimetric titration of a suspension of **a** 0.02813 and **b** 0.02905 g of vermiculite in 2.0 cm^3 of water with 0.50 mol dm^{-3} of butylamine **a** and hexylamine solution **b** in the same solvent at 298.15 ± 0.20 K. The experimental points represent the sum of the thermal effects of the amine titration ΣQ_{tit}, amine dilution ΣQ_{dil} and the net thermal effect of interaction ΣQ_r. ΣQ and ΣVad values are the sum of detected thermal effect and total injected volume of amine solution, respectively

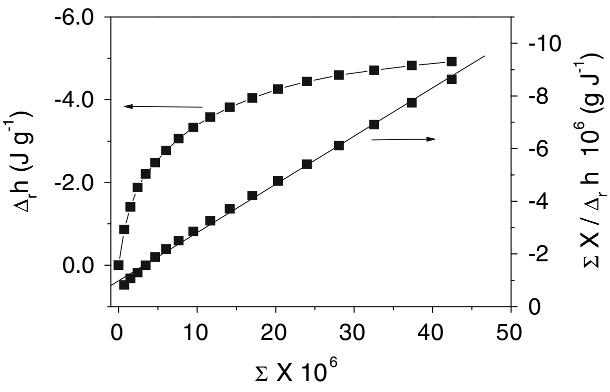

Fig. 4 Isotherm for the integral enthalpy of interaction ($\Delta_r h$) versus molar fraction (X) of amine obtained from a calorimetric titration of a suspension of solid in 2.0 cm^3 of water, with 0.50 mol dm^{-3} of ethylamine solution in the same solvent at 298.15 ± 0.20 K. The straight line is the linearized form of the isotherm

Table 2 Thermodynamic data for interaction between vermiculite and *n*-alkylamines in aqueous solution at 298 ± 0.02 K

$CH_3(CH_2)_nNH_2$	$-\Delta_{mon}H$ (kJ mol^{-1})	$-\Delta_{int}H$ (kJ mol^{-1})	ln K	$-\Delta G$ (J mol^{-1})	$+\Delta S$ (J mol^{-1} K^{-1})
$n = 1$	4.78 ± 0.005	7.72 ± 0.03	12.31	30.51 ± 0.3	77 ± 1
$n = 3$	0.72 ± 0.0003	1.9 ± 0.01	15.36	38.08 ± 0.1	121 ± 1
$n = 5$	5.46 ± 0.007	14.72 ± 0.06	12.24	30.09 ± 0.3	52 ± 1

intercalations for other inorganic matrices when interact with amines [17].

The reactions were investigated through calorimetric titration at the solid/liquid interface with the aim to obtain the thermodynamic parameters, due to the energetic of acid/base interaction. For this purpose the net enthalpy of reaction requires three independent series of measurements, where the lamellar solid, V–OH, in suspension interacts with the alkylmonoamine, RNH_2:

$$\begin{array}{ll} V{-}OH(susp) + RNH_{2(aq)} = V{-}O^{-}\,{}^{+}H_3NR_{(susp)}; & \Sigma Q_{tit} \\ V{-}OH_{(susp)} + nH_2O = V{-}OH.nH_2O_{(susp)}; & \Sigma Q_{hid} = 0 \\ RNH_{2(aq)} + nH_2O = RHN_2.nH_2O; & \Sigma Q_{dil}, \\ V{-}OH.nH_2O_{(susp)} + RHN_2.nH_2O & \\ \quad = V{-}O^{-}\,{}^{+}H_3NR_{(susp)} + 2nH_2O; & \Sigma Q_r \end{array}$$

The set of reactions represents the individual calorimetric measurements (Fig. 3).

The plot of $\Delta_r h$ as function of molar fractions of amine gives the angular and linear coefficients that determine $\Delta_{int}h$ and K, respectively, as illustrated in Fig. 4.

The set of thermodynamic data for reactions is listed in Table 2. The exothermic enthalpy data suggest a favorable acid-base reaction involving the OH groups of internal and external surfaces and basic nitrogen atoms of the *n*-alkylmonoamines.

From the equilibrium constant the Gibbs free energy values were calculated, which behavior was suggested a spontaneous reaction for this considered system. The calculated positive entropy data are consistent with the increasing in number of net free species in solution after reactions. As the interaction occurred in water, the solvent molecules can be disrupted from the solid or amine molecules as the reaction is going in progress. Thus, the inorganic matrix in suspension is solvated by water molecules, which are displaced to the solution as reaction takes place. The same behavior occurred with the solvated active nitrogen of amine that released water molecules to the medium after the interaction. Thus, the total contribution of these net free water molecules to the medium can cause an increase in entropy.

A suggestive behavior was observed for butylamine where lower enthalpy value was obtained (Fig. 3a and Table 2), contrasting with high value of Gibbs free energy and entropy. These data suggested a different mechanism of interaction between butylamine and vermiculite, possibly involving a multilayer formation, in which a lower enthalpy change was detected. On the other hand, this type of process is accompanied of high change in entropy due the displacement of water molecules through the various multilayer formations. In other words, the process is more favorable by entropy than enthalpy contributions. The lower enthalpy can be resulted from a different conformation of organic chain that it is not favorable to access the acidic sites of vermiculite.

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