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Crystalline lamellar ferric acid sulphate – intercalation of *n*-alkylmonoamines and thermochemistry

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Abstract

The crystalline compound ferric acid sulphate $FeH(SO)_4 \cdot 4H_2O$ (FHS) had its interlamellar gallery intercalated by a series of *n*-alkylmonoamines, $H_3C(CH_2)_nNH_2$ (n=1–7) from 1,2-dichloroethane (dce) and cyclohexane (cce) solutions. The intercalation was initially followed by a batchwise method at 298±1 K. The original interlamellar distance of 940 pm changed with the intercalated *n*-monoalkylamines. Thermogravimetric results showed that FHS lost H_2O in the first stage, H_2O plus SO_3 in the second step, to leave Fe_2O_3 as the residue. The intercalated compounds lost amines in the second step. The interlamellar distance d depends on the length of the aliphatic *n*-alkylmonoamine and is correlated to the respective number of the carbon atoms n_c in the aliphatic chain: $d=(947.23\pm13.25)+(121.96\pm2.63)n_c$. Linear correlations with good fits were obtained for the number of moles intercalated (n_{int}) as a function of n_c: $n_{int}=(14.00\pm0.13)-(0.84\pm0.02)n_c$ and $n_{int}=(11.15\pm0.13)-(0.57\pm0.02)n_c$ in dce and cce, respectively. The enthalpic values $\Delta_{int}H$ in kJ mol^{-1}, for the accomodation of the amines into the gallery were determined by reaction–solution calorimetry at 298.15±0.02 K. These values correlated with n_c, n_{int} and d, by means of the equations: $\Delta_{int}H=-(67.38\pm7.25)+(8.14\pm0.58)n_c$; $\Delta_{int}H=(47.18\pm5.26)-(9.68\pm1.02)n_{int}$; $\Delta_{int}H=-(133.35\pm15.12)+(0.07\pm0.01)d$; and $\Delta_{int}H=(40.92\pm7.45)-(8.48\pm1.05)n_{int}$; $\Delta_{int}H=-(53.75\pm9.87)+(6.02\pm1.78)n_c$ and $\Delta_{int}H=-(97.39\pm15.01)+(0.05\pm0.01)d$ for dce and cce, respectively. From these linear correlations the results suggest that enthalpic values can be inferred for other intercalated species. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: *n*-Alkylmonoamine; Intercalation; Ferric acid sulphate; Thermochemistry

1. Introduction

A great variety of crystalline inorganic compounds present lamellar properties. These ordered solids are organized in layers presenting special characteristics such as adsorptive functions, ion exchangers, molecular sieves, catalysts, ion and proton conductors and as convenient matrices for chemical modifications. On the other hand, an increase in application involving a series of this kind of materials is related to the their thermal and chemical stability, resistance to oxidation, selectivity to certain ions and molecules and so on [1].

One of the most important properties associated with this kind of layered materials is related to the expandable interlayer space for organizing guest species [1–3]. In such favourable conditions the inorganic matrix is prone to intercalation, which means the reversible insertion of a desired guest species into the layered host materials, where the main structural features of the inorganic framework is maintained [1]. Many natural or synthetic layered materials such as clay minerals [4], phyllosilicates [5], graphites [6],

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double hydroxides [7], crystalline silicic acids [8], polymer silicates [9], transition metal oxides [10], metal phosphates and phosphonate [1–3], etc. have been used as host materials for intercalation compounds. After intercalations new compounds are formed, whose properties as both guest and host can be altered by reactions, and in many cases, the resulting host–guest systems have been studied from the technological point of view. This change in interlayer distance can be followed by an X-ray diffraction technique, which can give information about the orientation and roughly estimate the disposition of the species in the gallery space [2,3,11].

The synthetic layered acid salts of tetravalent metals constitute an isostructural series of the general form $M(HPO_4)_2 \cdot H_2O$ (M=Zr, Ti, Si, Ge, Sn, Pb, Hf, etc.), where microcrystals arise from the packing of layers. Each layer is constituted by concatenation through the vertices or the corners of the tetrahedrons or octahedrons [12,13]. In this arrangement one phosphate group is bonded to a proton which is located in the interlayer gallery, where the water molecule is hydrogen bonded and the layers are only weakly held together by dispersion forces in an extensible two-dimensional space [1–3]. Thus, the resulting active sites on the support interact with the molecules of the intercalating agent to establish a stoichiometric composition, when the active sites are exactly covered by the guest molecule [14–17].

During molecule insertion an interactive reaction occurs due to the entrance of the species into the free space of the gallery. A knowledge of this feature contributes significantly to the understanding of the behaviour of the lamellar compounds, because any phenomenon which can affect the interlayer distance always produces thermal effects [18–20]. Thus, the energetics of intercalation can be known through calorimetric techniques in a heterogeneous system. The determined interactive energetics of this effect is due to an acid–base enthalpic value obtained between the guest molecule and the host of the inorganic matrix. This behaviour has been focused upon with some *n*-alkylmono- [18] and *n*-alkyldiamines [19] with α-titanium hydrogenphosphate. For this interaction the proposed mechanism indicates that the basic nitrogen group in both series of amines is supposed to be first protonated by the free hydrogen of the phosphate group. In both systems a linear behaviour was established between the enthalpic values with the interlamellar distance or with the number of carbons in the aliphatic chains. From these linear correlations the enthalpic values can be inferred for other non-intercalated species by using the number of carbons in the organic moiety molecule or by considering the interlamellar distance [18,19].

The purpose of this publication is to report a contribution on the energetics of intercalation *n*-alkylmonoamines of the general formula $H_3C(CH_2)_n$-NH_2 (n=1–7) into the lamellar space available in the crystalline structure of ferric acid sulphate, $FeH(SO_4)_2 \cdot 4H_2O$ [21]. Due to the great facility of the lamellar compound in hydrolysing, the intercalation by a batch method or in a calorimetric vessel was followed in 1,2-dichloroethane (dce) or cyclohexane (cce) as solvents. The acquisition of some thermochemical values will contribute with the scarce data available and correlations involving some properties will also enrich an understanding of the energetics of intercalation.

2. Experimental

2.1. Reagents

All chemicals used were of reagent grade. Demineralized water was used throughout the preparative experiments. Ferric sulphate nonanhydrate (Fluka) and sulphuric acid (Merck) were used for the preparation of the lamellar compound. For intercalation, normal primary aliphatic monoamines (Aldrich) of the general formula $H_3C(CH_2)_nNH_2$ were used. Thus, ethyl (eta), propyl (ppa), butyl (bta), pentyl (pta), hexyl (hxa), heptyl (hta) and octyl (oct) correspond to n varying from 1 to 7. The non-aqueous solvents 1,2-dichloroethane (dce) and cyclohexane (cce) were used without further purification.

2.2. Preparation

The lamellar ferric acid sulphate was prepared by reacting 25.0 cm^3 of a solution containing 20.0 g of ferric sulphate with 8.0 cm^{-3} of 18.0 mol dm^{-3} sulphuric acid at room temperature [22]. The solid was slowly formed and after a week the pale yellow crystalline solid was washed with dry acetone and dried in vacuo at 353 K. The amount of iron(III) in final product was determined by EDTA batch-titration, after adding a standard zinc solution [23]. The result obtained 17.30% for these analyses is in good agreement with the expected value of 17.40% for the proposed general formulae $FeH(SO_4)_2{\cdot}4H_2O$, hereafter called FHS.

2.3. Intercalation

The intercalation of all normal aliphatic monoamines at 298±1 K was followed batchwise in non-aqueous solution due to the great ability that the matrix has in hydrolysing. In this procedure each individual amine was dissolved in 1,2-dichloroethane (dce) or cyclohexane (cce), whose concentration was previously determined by titration with a 0.10 mol dm^{-3} hydrochloric acid solution, after diluting samples of these solutions in water. Samples of FHS were suspended in various concentrations of amine in the chosen solvent in polyethylene flasks, having a proportion of 0.15 g of solid per 25.0 cm^3 of amine solution. The system was mechanically stirred [18,19]. In a first stage, the time required to reach the equilibrium was first established by considering a series of intercalations involving a constant mass of the lamellar compound with the amines as a function of time. By running 20 h of experiments, the resulted isotherm gave an indication that 5–6 h were sufficient to attain the equilibrium and 20 h was chosen to ensure the maximum intercalation. At the end of this time, the solid was separated by filtration and dried at room temperature in vacuo. From the titration of the supernatant with hydrochloric acid, the amount of the amine intercalated (n_{int}) can be determined by the expression: $n_{\mathrm{int}}=(n_{\mathrm{i}}-n_{\mathrm{s}})/m$, n_{i} being the initial number of moles of amine added to the solution, n_{s} the number of moles of amine in solution in equilibrium with the solid phase and m the mass of the lamellar compound [18–20]. For each experimental point, the reproductibility was checked by at least a triplicate run.

2.4. Analytical procedures

The loss of mass determinations were performed on a DuPont model 2000 thermogravimetric instrument coupled with a model 951 thermobalance, with samples varying in mass from 7.0 to 15.0 mg. The curves were obtained by using a flux of dry nitrogen at a heating rate of 0.167 K s^{-1}. X-ray powder patterns were obtained with nickel-filtered Cu K_α radiation on a Shimadzu model XD3A diffractometer and the interlayer spacing of the compounds were calculated from the (0 0 2) plane. The infrared spectra were obtained on a Perkin-Elmer FT-IR 2200 spectrometer with solid samples ground to obtain a pulverized material.

2.5. Calorimetry

An LKB 8700-1 isoperibolic precision calorimetric system or a Thermometric 2225 precision solution calorimeter were used for all reaction–solution measurements of the intercalation of amines into lamellar ferric acid sulphate in dce and cce media. The thermal effects caused by breaking thermostated thin-glass ampoules containing the matrix FHS (ca. 120 mg) in 0.10 dm^3 of amine solutions of variable concentration and the corresponding heat produced were recorded. The response of breaking of the ampoules in the well-stirred solution indicated a kinetically favourable system, where the baseline was reached rapidly in a few minutes. As observed with other lamellar compound, no heat was observed when only FHS samples were broken into the calorimetric solvent [18,19]. The standard molar enthalpies of intercalation were obtained by breaking at least five ampoules at 298.15±0.02 K. The heat of empty ampoule breaking was found to be negligible [24,25]. The same procedure was used with the thermometric system, where Sol Cal software was used to calculate the enthalpy, which was given by considering the heat of breaking divided by the number of moles intercalated [18,19]. The results obtained in both calorimetric systems showed identical values. At the end of this operation, the resulting solution was filtered and aliquots of supernatant were titrated with standard hydrochloric acid solution to obtain n_{int} values. For each determination, the isolated solid was dried and submitted to infrared and X-ray measurements.

3. Results and discussion

A distinguisable property of layered compounds is related to the existence of a two-dimensional expandable interlayer space, which gives conditions to accomodate a variable amount of guest polar molecules. The normal structural arrangement of this kind of compounds consists of inorganic layers with a gallery between them, and as a consequence of the method of preparation, this void is partially occupied by water molecules [1,3,26]. In the case of the lamellar matrix iron hydrogensulphate, $FeH(SO)_4{\cdot}4H_2O$, the inorganic layers are formed by iron and sulphate [21,27,28], and the free space is occupied by diaquahydrogen ions [29], the species responsible for proton transfer properties [30–32] and for hydrogen bond formation [21,28] with the insertion of a given molecules, due to its basic centre. During the intercalation of a basic molecule the layered structure is maintained and the proton is transferred in a non-redox reaction [21,28].

The sequence of layers is only weakly held together by dispersion forces. The interlayer distance determined was 940 pm [21,27,28]. However, this distance can be altered when the host layer interacts with the organic guest molecules in a typical acid–base reaction. In this process the fully intercalated material consists of regularly alternating organic and inorganic layers with a significant modification of the original physical and chemical properties [19]. For the sequence of the *n*-monoalkylamines, the intercalation was followed by a titration technique and the results are shown in Table 1. The series of *n*-alkylmonoamines showed that the number of moles intercalated n_{int} decreases with an increase in the chain length of the amine, as can be illustrated by ethyl- and octylamines, which changed from 10.1 to 5.1 mmol of amine per gram of the matrix for intercalation in dce solvent. Similar results were found for both amines 9.5 and 5.2 mmol g^{-1} were found for the same process in cce solvent, respectively. The explanation for this large contrast can be correlated with the size of the *n*-alkyl chain. So, larger amines have less freedom to diffuse into the interlayer space to interact with the acid site distributed in the inorganic layer, or larger volume can fill out the available lamellar space of the support. Thus, octylamine is supposed to have the lowest intercalated value for this considered series.

Table 1
The number of moles of *n*-alkylmonoamines, $H_3C(CH_2)_nNH_2$ (n=1–7), intercalated n_{int} and the respective interlamellar distance, *d*, after intercalation into the lamellar $FeH(SO_4)_2{\cdot}4H_2O$

Amine	n_{int} (mmol g^{-1})		*d* (pm)
	dce	cce	
eta	10.1	9.5	1176
ppa	9.4	8.9	1282
bta	8.6	8.6	1434
pta	7.5	8.0	1572
hxa	6.6	6.4	1688
hta	6.1	6.7	1804
oct	5.1	5.2	1919

The original lamellar compound and the intercalated compounds are sensitive to heating. This behaviour was followed by thermogravimetry [18]. Thus, FHS presented a loss of mass in two distinct steps. In the first one, 42.9% was lost in the range 370–520 K, due to the elimination of water. In the next step, a loss of 33.3% in the range 920–990 K was observed, which can be attributed to the decomposition of the anhydrous lamellar compound to produce water and sulphur trioxide, and leaving ferric oxide as the residue. As expected, this residue was observed for other similar compounds [33]. The total mass loss corresponds to the presence of four molecules of water per mole of lamellar compound. Based on the total mass lost and the iron elemental analysis determination, the general formulae for the lamellar compound can be established as: $FeH(SO_4)_2{\cdot}4H_2O$ and the steps of decomposition lead to

$$2FeH(SO_4)_2 \cdot 4H_2O(c) \rightarrow 2FeH(SO_4)_2(c) + 8H_2O$$

$$2FeH(SO_4)_2(c) \rightarrow Fe_2O_3(c) + H_2O(g) + 4SO_3(g)$$

A similar profile of thermogravimetric curves is observed for all intercalated compounds. Water and amine were lost in the range of temperature between 370 and 650 K to give the anhydrous matrix, which suffers decomposition as before, to leave ferric oxide as residue.

X-ray diffractometric results gave additional information not only about the interlamellar distance, but also relating to the disposition of the guest molecule into the gallery [27]. Thus, the initial interlamellar distance increased with the chain of the *n*-alkylmonoamine intercalated, as observed in Table 1. Data for amines intercalated in metal hydrogenphosphate compounds indicate that the alkylchains rest at an inclined angle with respect to the plane of the inorganic layer.

Then, the inclination increases from the position of the N–C bond which turns out to be nearly perpendicular to the inorganic layer [27,34]. In the present case, the way of intercalation of the series of *n*-alkylmonoamines is very close to that found with other matrices [18,27,34]. Thus, the same criterion to calculate the alkylchain inclination was applied. For the disposition of the *n*-alkylmonoamines in a *trans–trans* conformation, a length of 153 pm is attributed for any atom of additional carbon in the chain. The disposition of the amine into the gallery with respect to the inorganic layer has its axial axis inclined on an average, arcsin(126/153)=52.8°, where the value 126 pm was obtained from the slope of the linear correlation (Eq. (1)) between the interlamellar distance and the number of carbons in the amine aliphatic chain, n_c, as shown in Fig. 1. In the following expression R is the linear coefficient of correlation:

$$d = (947.23 \pm 13.25) + (121.96 \pm 2.63)n_c, \quad R = 0.999. \tag{1}$$

The alkylchain inclination of 52.8° for the present series of *n*-monoamines has the same reported value for similar sequence of amines with metal hydrogenphosphate matrices [1,3,27]. This found angle is very close to the proposed model of arrangement for these molecules into the gallery, which value of 53.8° can be expected. This well-behaved system presented correlations related to the number of moles of amines n intercalated for dce and cce solutions, as illustrated in Fig. 2(a) and (b). These results conformed linearly with n_c values, as shown in the following equations:

$$n_{int} = (14.00 \pm 0.13) - (0.84 \pm 0.02)n_c, \quad R = 0.998 \text{ (dce)}. \tag{2}$$

$$n_{int} = (11.15 \pm 0.13) - (0.57 \pm 0.02)n_c, \quad R = 0.997 \text{ (cce)}, \tag{3}$$

The infrared Fourier-transform spectra for the lamellar inorganic matrix and the respective series of the intercalated compounds showed the presence of characteristic bands at 3400 and 1655 cm^{-1} attributed to asymetric and symmetric O–H stretch vibrations, respectively, demostrating the presence of water molecules into the lamellar space. The peaks at 1120 and 613 cm^{-1} correspond to the presence of the S–O stretching modes of vibration of the sulphate anion

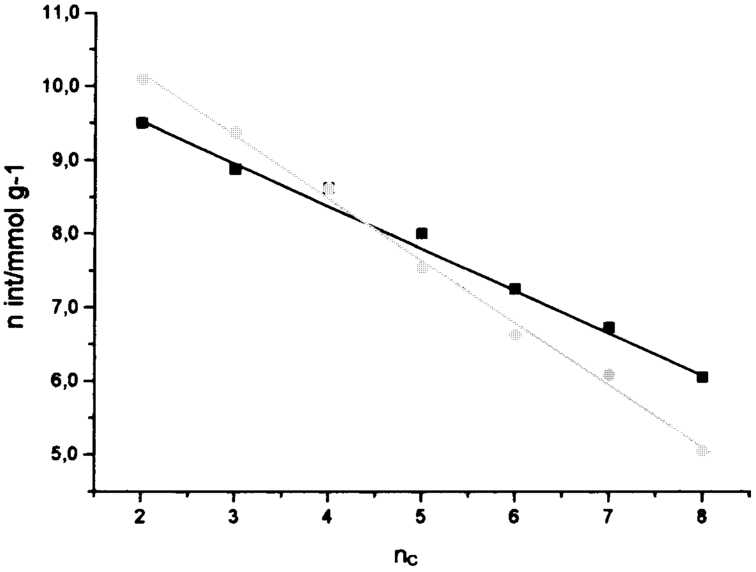

Fig. 1. Number of moles intercalated n_{int} as a function of the number of carbons n_c of *n*-alkylmonoamines, $H_3C(CH_2)_nNH_2$(n=1–7), from 1, 2-dichloroethane (dce) and cyclohexane (cce) solutions.

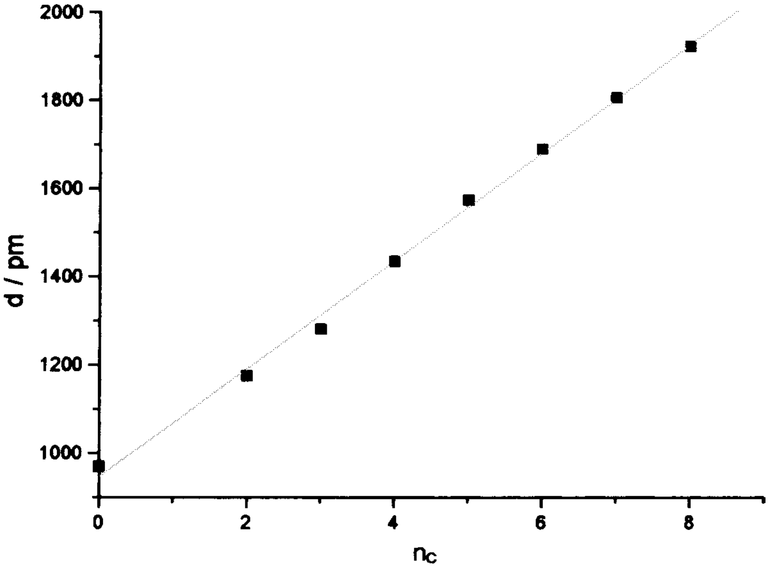

Fig. 2. Interlamellar distance d after intercalation as a function of the number of carbons of n-alkylmonoamines n_c.

[35]. After intercalation the infrared peaks of water showed a remarkable decrease in intensity. On the other hand, a drastical change in spectra occurred due to the presence of the intercalated n-alkylmonoamine molecules. In this process, the water molecules in the gallery of the lamella is partially substituted by amines, as is clearly observed by the presence of N–H stretching vibration peaks. So a sequence of peaks corresponding to antisymmetric and symmetric NH_3^+ stretching, NH_3^+ deformation, NH_3^+ symmetric deformation, and NH_3^+ rocking vibrations, appear in the regions 3400–3000, 1650–1550, 1370–1000, and 950–590 cm^{-1}, respectively [28,35]. Another point to be observed in this set of spectra is related to the decrease of the intensity of these series of peaks as the number of carbons in the alkyl chain increases.

In an attempt to acquire information about the thermodynamics of intercalation, a series of organic molecules interacted with the inorganic matrix in the organic solvent and the respective enthalpic values were obtained by means of reaction–solution calorimetry [18–20]. All the data obtained in this heterogeneous process of intercalation can be interpreted as an acid–base solid-state reaction between a suspension of the layered acid and the Lewis base. The molar enthalpy of intercalation of n-alkylmonoamines in two different aprotic organic solvents are listed in Table 2, as well as the number of runs for each specific determination. The results show that in both solvents, an increase in the number of carbon atoms in the series of alkyl, the chain caused a decrease in the exothermicity of the enthalpies of intercalation. This fact is well illustrated by comparing the enthalpic values obtained with the amines considered. The shortest aliphatic n-alkylmonoamine chain eta gave the enthalpic values of intercalation of −56.24±0.58

Table 2
Values of enthalpy of intercalation $\Delta_{int}H$ of n-alkylmonoamines $H_3C(CH_2)_nNH_2$ (n=1–7) in 1,2-dichloroethane (dce) and cyclohexane (cce) media for five independent determinations

Amines	$-\Delta_{int}H$ (kJ mol^{-1})	
	dce	cce
eta	56.24±0.58	39.95±0.49
ppa	43.38±0.17	34.78±0.14
bta	31.24±0.22	28.52±0.06
pta	27.58±0.12	18.99±0.10
hxa	15.59±0.04	13.50±0.27
hta	9.04±0.04	8.29±0.05
oct	2.41±0.01	3.50±0.05

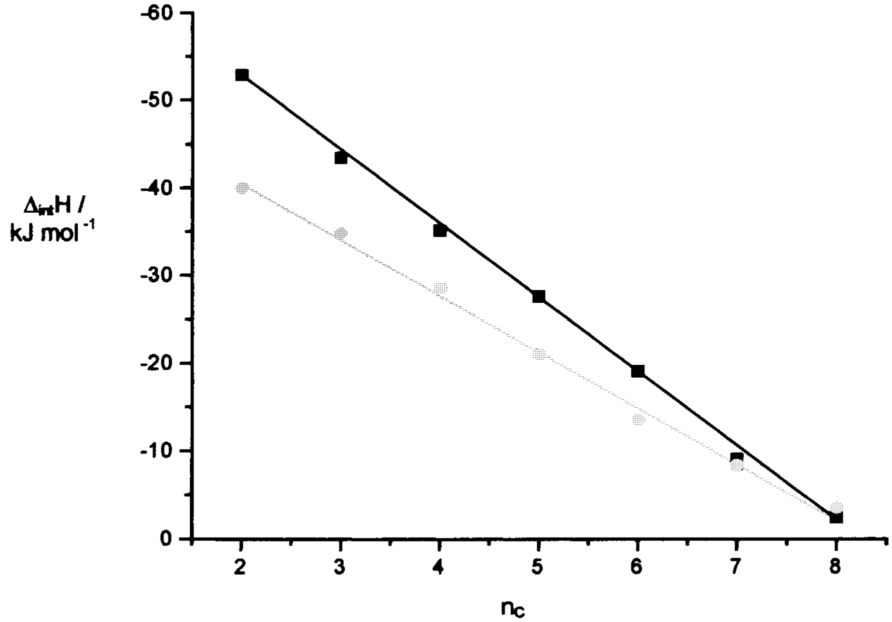

Fig. 3. Standard enthalpy of intercalation $\Delta_{\mathrm{int}}H$ of *n*-alkylmonoamines, $H_3C(CH_2)_nNH_2$ (*n*=1–7), into $FeH(SO_4)_2{\cdot}4H_2O$ from dce (■) and cce (●) solutions as a function of the number of carbons n_c.

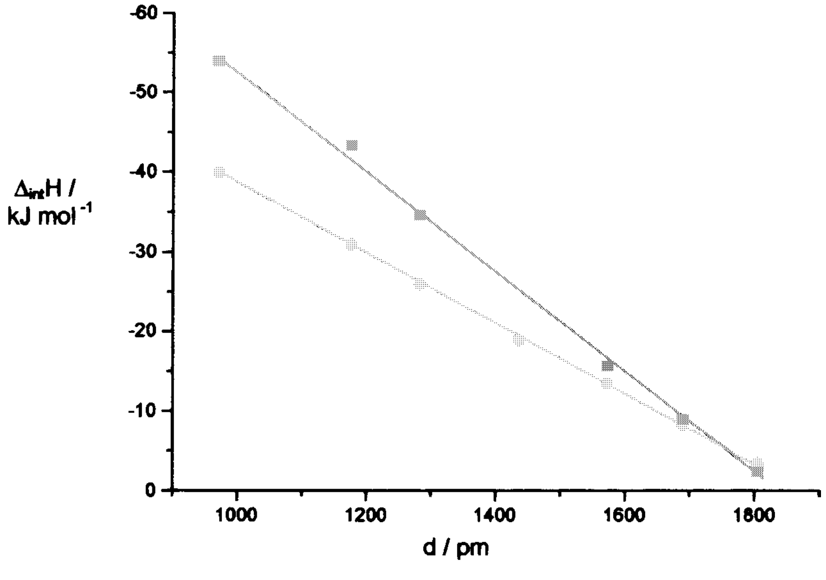

Fig. 4. Standard enthalpy of intercalation $\Delta_{\mathrm{int}}H$ of *n*-alkylmonoamines, $H_3C(CH_2)_nNH_2$ (*n*=1–7), into $FeH(SO_4)_2{\cdot}4H_2O$ from dce (■) and cce (●) solutions as a function of the interlamellar distance *d*.

and -39.95 ± 0.49 kJ mol^{-1} in dce and cce, respectively. These values contrast with those of the largest octylamine -2.41 ± 0.01 and -3.50 ± 0.05 kJ mol^{-1}, respectively, for the same sequence of solvents. As observed before, these molar enthalpies of intercalation $\Delta_{\mathrm{int}}H^0_{\mathrm{m}}$ in kJ mol^{-1} correlated linearly with the number of carbons of the *n*-alkylmonoamines, n_c, n_{int} and also with the interlamellar distance, *d*, as illustrated in Figs. 3 and 4, respectively. Those for dce are:

$$\Delta_{\mathrm{int}}H = -(67.38 \pm 7.25) + (8.14 \pm 0.58)n_{\mathrm{c}},$$
$$\Delta_{\mathrm{int}}H = (47.18 \pm 5.26) - (9.68 \pm 1.02)n_{\mathrm{int}}$$
$$\Delta_{\mathrm{int}}H = -(133.35 \pm 15.12) + (0.07 \pm 0.01)d,$$

and for cce are:

$$\Delta_{\mathrm{int}}H = -(53.75 \pm 9.87) + (6.02 \pm 1.78)n_{\mathrm{c}},$$
$$\Delta_{\mathrm{int}}H = (40.92 \pm 7.45) - (8.48 \pm 1.05)n_{\mathrm{int}},$$
$$\Delta_{\mathrm{int}}H = -(97.39 \pm 15.01) + (0.05 \pm 0.01)d.$$

From the collected thermochemical data it is evident that the contribution to enthalpy by each carbon added to the aliphatic chain of the *n*-alkylmonoamine, corresponds to a decrease of 6.02 kJ mol^{-1} in cce and 8.14 kJ mol^{-1} in dce. In terms of the variation in interlamellar spacing, this corresponds to 106 pm for each carbon added to the aliphatic chain. In extrapolating the linear behaviour of these correlations to null carbon atom n_{c}=0, the enthalpy of intercalation of 1 mol of ammonia per mole of inorganic matrix has a value of −54.69 and −43.10 kJ mol^{-1} for dce and cce, respectively. The sequence of enthalpies determined here with a limited number of *n*-alkylamines contributes to the understanding of these types of system. The linear correlations observed suggest that the enthalpic values can be followed for other intercalated species. These linear correlations for *n*-alkylmonoamines can be used to estimate properties from the number of carbons in the alkyl chain or through the interlamellar distance.

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