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Intersalation Reactions of Trisdiimine Metal Complexes with Montmorillonite Clay: A New Approach

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Intersalation reactions of the complexes $[Ni(L\text{-}L)_3]SO_4$ and $[Ni(L\text{-}L)_3]Cl_2$ (L-L = 1,10-phenanthroline (phen), 2,2′-bipyridyl (bpy)), with Na–montmorillonite carried out under different dynamic conditions such as ultrasonic irradiation, refluxing, autoclaving, and vigorous stirring showed that under ultrasonic irradiation, maximum adsorption of the metal complexes occurred within a period of 30 min. Metal complexes containing the phen ligand showed higher adsorption than those containing bpy. Maximum adsorption up to about three times the cation exchange capacity (CEC) of the clay was observed. Aggregated (basal spacing d_{001} 12.5 Å) Na–montmorillonite, in treatment with a higher amount (>CEC) of metal complexes, formed monolayered (basal spacing d_{001} 17.6 Å) species, while with predispersed clay, bilayered (basal spacing $d_{001} > 28$ Å) or pseudo-trilayer (basal spacing $d_{001} > 32$ Å) species were formed. The bilayered species were thermally stable up to 250°C and above this temperature monolayered species were formed. The thermal stability of the intersalated species was higher than that of the intercalated ones. X-ray diffraction, UV-visible, IR-spectroscopy, thermal analyses, and surface area measurements were used for characterization of the products. © 2001 Academic Press

Key Words: **intersalation; intercalation; montmorillonite; ultrasonic irradiation; interlamellar spacing; dispersion; monolayered; bilayered; pseudo-trilayer.**

INTRODUCTION

Recent advances in the intercalation and intersalation (accommodation of ion-pair salt into the interlamellar region) reactions of metal complexes or other organic compounds with montmorillonite clay have paved the way for the development of new classes of supported (heterogeneous) catalysts, bioactive agents, chemical sensors, slow release materials, adsorbents, etc. (1–8). The intercalation reaction of guest species into the interlamellar space primarily occurs through (i) cation exchange with interlayer exchangeable cations and (ii) ion–dipole interactions with the interlayer cations and/or hydrogen bonding with the surface oxygen atom of the silicate sheets. Most of the intercalation reactions have been carried out in solid–liquid or solid–gas reactions. Recently, solid–solid intercalation reactions between metal complexes and Na–montmorillonite have successfully been carried out (9). Literature reports reveal that the intercalation reaction between metal complexes and montmorillonite is slow and takes a long time to reach equilibrium and, in most cases, the total reaction time required is from a few hours to a few days (3, 10, 11). Any industrial application of such metal-complex intercalated/intersalated products (12) will require precise and viable methods for preparation of the same. Moreover, in the adsorption study of optically active metal complexes (5, 10, 13–15), long intercalation reaction times may be detrimental for investigating the reaction mechanism as well as the products because of the short racemization period of most enantiomeric species (16). Again, from the environmental and industrial point of view for separation of toxic metal complexes, the intersalation reaction may play a significant role. A systematic study on the preparation of metal-complex intercalated/intersalated montmorillonite composites has not been performed so far. In view of the above, an attempt has been made to curtail the total intercalation/intersalation reaction period and also to simplify the reaction procedure by applying different dynamic conditions like ultrasonication, refluxing, autoclaving, and vigorous stirring (17). The present paper describes the results of the interaction between Na–montmorillonite and the metal complexes $[Ni(L\text{-}L)_3]SO_4$ and $[Ni(L\text{-}L)_3]Cl_2$, particularly the effect of the intersalation reaction on interlamellar metal-complex layer formation. The intercalated and intersalated composites have been characterized by X-ray diffraction, TGA, DTG, DTA analyses, infrared spectroscopy, and surface area measurement.

MATERIALS AND METHODS

Sample Preparation and Instrumental Technique

Na–montmorillonite clay (M/S Neelkanth Sodaclays and Pulverisers, Jodhpur, India) was purified by a sedimentation technique (18) into separate 2-μm fractions and then converted to Na–montmorillonite form by overnight shaking with 1 M NaCl. The slurry was washed with distilled water several times and allowed to settle. The clear supernatant liquid was decanted and the slurry was dialyzed, in order to remove excess NaCl, in a

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TABLE 1
Oxidic Composition (wt%) of Clay

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	LOI
59.42	20.02	4.43	1.55	0.69	2.82	0.09	11.02

synthetic dialysis bag (pore size 0.2 μm) until the washings showed a negative chloride test with $AgNO_3$ and the conductivity was below 20 μS/cm. The dialyzed product was dried in a flat dish in an air oven at 50 ± 5°C for about 48 h to obtain flakes of the clay. An ethylene glycol adsorption test was carried out and the basal spacing determined by the X-ray diffraction method was found to be 16.5 Å, indicating a characteristic value for Na–montmorillonite intercalated with ethylene glycol (19). The chemical composition of the clay is shown in Table 1. The cationic exchange capacity (CEC) of the clay determined by the ammonium acetate method or the calcium substitution method (20) was found to be 114 Meq/100 g clay. $[Ni(L\text{-}L)_3]SO_4$ and $[Ni(L\text{-}L)_3]Cl_2$ complexes were prepared by standard methods from metal salts and appropriate ligands (21). Intersalated/intercalated products were characterized by XRD (Cu$K\alpha$ radiation, Jeol, JDX-11P3A, X-ray diffractometer, Japan) by determining the basal spacing (d_{001}) from the oriented film prepared on a glass slide using the standard method (22), i.e., a drop of thick well-dispersed slurry of the adsorbed product was put on a glass slide and allowed to dry undisturbed at room temperature for about 24 h. XRD patterns (2θ: 2–60°) were then obtained. Infrared spectra (400–4000 cm^{-1}) of the samples were taken as a KBr pellet on a FTIR spectrophotometer (Perkin–Elmer). The concentrations of the metal complex before and after the adsorption reactions were determined with the help of a UV-visible spectrophotometer (Shimadzu, UV-160A, Japan), using the absorption band near 520 nm. Thermal stability of the products was studied by TG, DTA, etc. (TA Instrument, Model SDT 2960, Simultaneous DTA-TGA) and also by heating the oriented film slide at 100, 250, 350, 450, 550, and 650°C in an air oven for 1 h. The surface area (m^2/g) was determined (Coulter SA 3100) by the BET method.

Adsorption (Intercalation/Intersalation) Reactions

(a) Under ultrasonic irradiation. About 50 mg of finely ground clay (dried at 50 ± 5°C) was directly added to each 10-ml solution containing 0.1, 0.5, 1.0, 2.0, and 4.0 CEC Eqv of metal complexes. Alternately, 50 mg of clay was dispersed in 10 ml of water under ultrasonic vibration for about 10 min and the respective metal complex solution was added to it. The whole mass was ultrasonicated under closed conditions for 30 min with the help of an ultrasonic bath (Julabo Labortechnik, Type USR 1/2 905, HF freq 35 KHz). In another experimental condition, 50 mg of finely ground clay (dried at 50 ± 5°C) was directly added to 10 ml of solution containing 4.0 CEC Eqv of metal complex and ultrasonicated under closed conditions from 1 to 60 min. The clay-adsorbed products were filtered through a sintered bed under mild suction and the filtrate was analyzed for unadsorbed metal complex. The residue was washed thoroughly with distilled water and dried at 50 ± 5°C in an air oven.

(b) Under refluxing conditions. Dry clay or slurry of it was directly added to the solution of metal complexes (as described above) and the mass was refluxed at about 100°C under stirring conditions for about 30 min, followed by filtration and drying as above.

(c) Under autoclaving conditions. Dry clay or slurry of it was added directly to the metal complex salt solution (as above) and was autoclaved in a closed steel reactor lined with Teflon at 120°C (at 2 atm pressure) for a peiod of 30 min under rolling conditions in a roller oven (Chromalox, OFI, Testing Equipment USA, Part No. 17300, Serial No. 87-38). Under another experimental condition, 50 mg of solid clay was directly added to 10 ml of solution containing about 4 CEC Eqv of $[Ni(phen)_3]SO_4$. The mass was autoclaved separately in a closed Teflon-coated pressure reactor (Model HR 100, Berghof, Germany) for 30 min at 80, 90, 100, 110, and 120°C (corresponding pressure 0.5, 0.7, 1.0, 1.4, and 2.0 atm). The adsorbed products were then washed and dried as above.

(d) Under vigorous stirring. Dry clay or slurry of it was added directly to the metal complex salt solution (as above) and the whole mass was vigorously stirred under closed conditions with the help of a magnetic stirrer for about 30 min and then filtered and dried as above.

RESULTS AND DISCUSSION

The details of the intersalation reaction, i.e., adsorption of metal complex salts in excess (>CEC) by the clay (slurry), are shown in Fig. 1. They reveal that the highest amount of metal complex adsorption occurs under ultrasonic conditions, while under stirring conditions the lowest adsorption is found. Adsorption under refluxing conditions is higher, in general, than under autoclaving, except in some cases. Therefore, the sequence of adsorption at higher loading (>CEC) is ultrasonication > refluxing > autoclaving > stirring. Under ultrasonic conditions, adsorption of $[Ni(phen)_3]SO_4$ and $[Ni(phen)_3]Cl_2$ was 2.9 and 2.5 CEC Eqv, respectively, when the dispersed clay was treated with 4 CEC Eqv of the metal complexes. On the other hand, under the same conditions of treatment, the complexes $[Ni(bpy)_3]SO_4$ and $[Ni(bpy)_3]Cl_2$ show adsorption of 2.1 and 1.9 CEC Eqv, respectively. Similar observations are noticed in the case of 2 CEC Eqv treatment. Thus, the phen-containing complex, irrespective of its anions, shows a higher adsorption on the clay surface than the bpy-containing one. This difference in adsorption can be attributed to the more rigid structure of the phen-containing metal complex compared to that of bpy, which leads to more efficient packing (5a, 10a, 23) in the interlamellar spacing of the clay.

In the intersalation reaction the excess (>CEC) adsorption is considered due to the intermolecular interaction and a van der Waals-type attraction between the metal complex salts caused

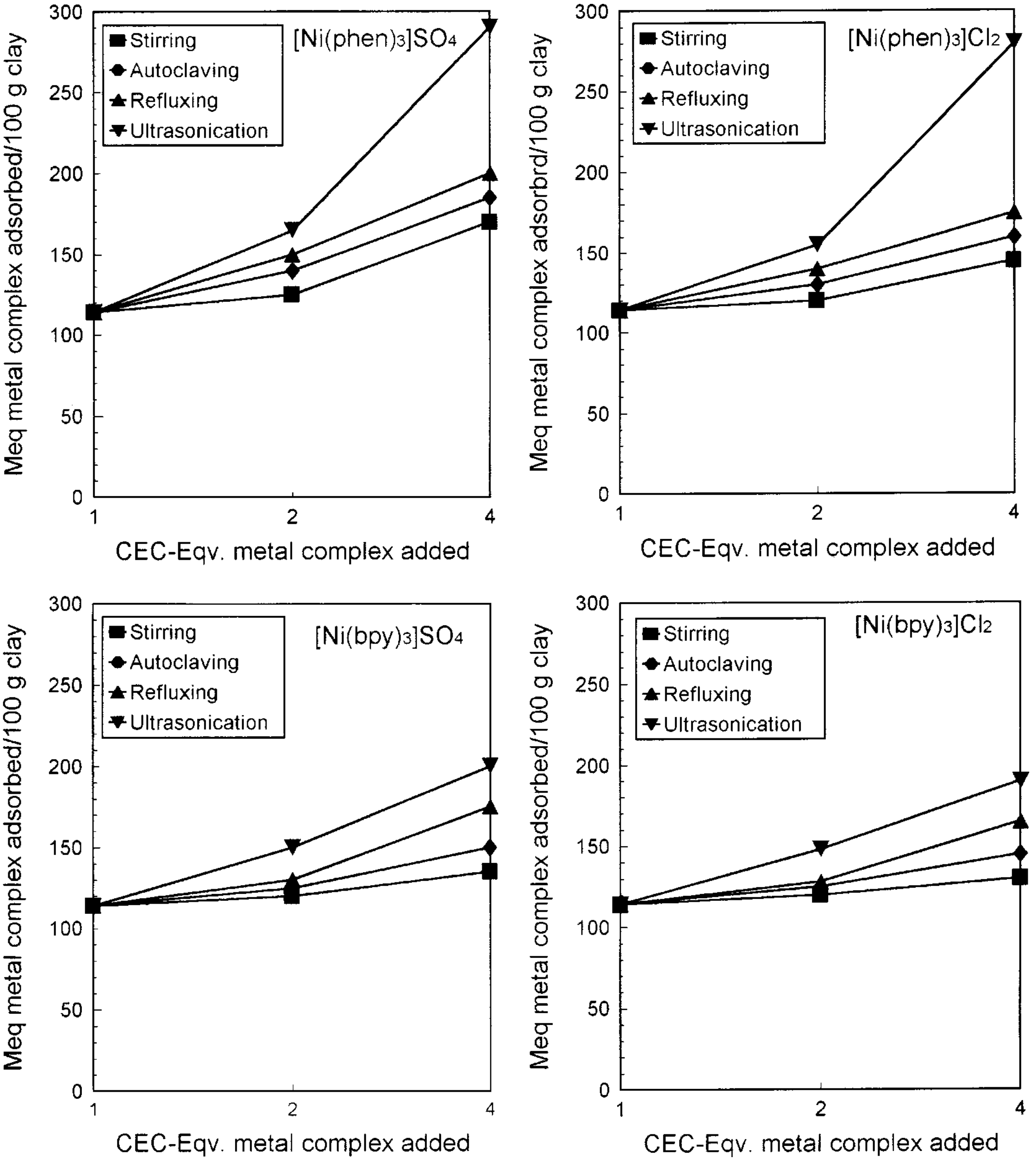

FIG. 1. Adsorption isotherm of $[Ni(phen)_3]SO_4$, $[Ni(phen)_3]Cl_2$, $[Ni(bpy)_3]SO_4$, and $[Ni(bpy)_3]Cl_2$ on Na–montmorillonite (heated at 100°C for 1 h).

by the closeness of the adsorbates in the clay interlayers (5a, 13, 24, 25).

The anion has a profound influence on the amount of adsorption in the present study. The SO_4^{2-} ion-containing complex show higher adsorption than Cl^--containing ones (3a). This may be due to the greater ability of SO_4^{2-} ions to order the intersalated phases and compensate simultaneously the excess positive charge caused by adsorption beyond CEC (26). In addition, the greater tendency of ion pairing of the SO_4^{2-} ion compared to the Cl^- ion increases its ability to intersalate (5a, 27).

It is known that ultrasonication increases the rate of intercalation and other types of reactions (11a, 28). In the case of the intersalation reaction of $[Ni(phen)_3]SO_4$ and $[Ni(bpy)_3]SO_4$, it is found that ultrasonication leads to maximum adsorption during 25–35 min, but beyond this point, desorption occurs (Fig. 2). The amount of adsorption of $[Ni(phen)_3]SO_4$ for 1 and 60 min is almost same and is slightly higher than that of CEC, but in case of $[Ni(bpy)_3]SO_4$ the adsorption is below the CEC. Therefore, the intersalation reaction is dependent on the ultrasonication period and there is a critical time period for maximum adsorption; beyond that region on either side, the adsorbed amount is less. Thus, adsorption under ultrasonication conditions is of the reversible type.

The results of adsorption by the aggregated (solid) and dispersed clays carried out under vigorous stirring conditions are shown in Table 2. Results indicate that dispersed clay, in general,

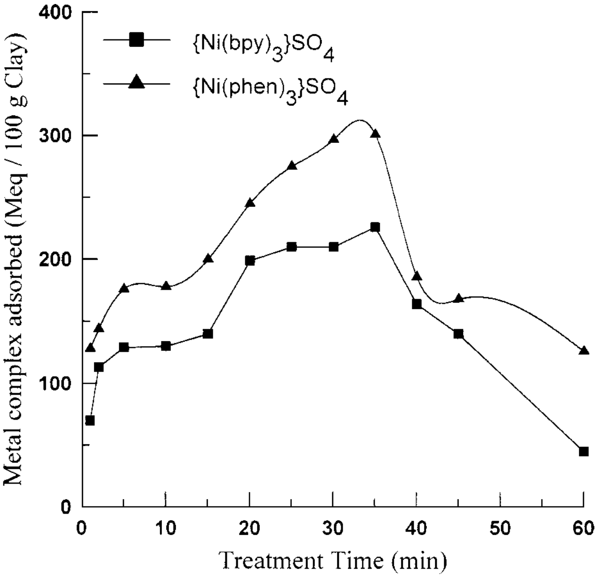

FIG. 2. Adsorption isotherm of $[Ni(phen)_3]SO_4$ and $[Ni(bpy)_3]SO_4$ on Na–montmorillonite carried out under ultrasonic irradiation for different periods.

adsorbs a higher quantity of metal complexes than the undispersed clay. In order to simplify the reaction conditions, room temperature dried clay (basal spacing d_{001} 12.5 Å, i.e., interlayer space of about 2.9 Å corresponding to the presence of a monolayer of water between the layers and, as per Eq. [1], the attractive energy is 6.7 mJ/m^2) was directly added to the metal complex salt solution and the adsorption reaction was carried out. The clay adsorbs very quickly up to the CEC and within a few minutes the reaction is over, irrespective of the concentration (<CEC) of the metal complex. The basal spacing (d_{001}) of such products derived either from solid or slurry of clay is enhanced from 12.5 to about 17.6 Å, indicating that the cation of the metal complex, having diameter about 8 Å, exists in the interlamellar spacing with its threefold axis perpendicular to the silicate layer surface. When the clay (solid) is treated with a metal complex in excess (>CEC), the amount adsorbed is higher than the CEC. This excess adsorbed amount depends upon the reaction conditions as well as the treatment dose. The intersalated products, irrespective of amount adsorbed, show basal spacing of about 17.6 Å, confirming a monolayer product (3). Therefore the excess (>CEC) metal complex salt is assumed to exist laterally in the interlamellar spacing as a cation–anion pair between the exchanged metal-complex cations since the distance between the exchanged charge sites on the same silicate layer is about 10–15 Å (29).

TABLE 2
Adsorption of Metal Complexes by Na–Montmorillonite (under Vigorous Stirring)

	Metal complexes added (CEC eqv)					
	1.0		2.0		4.0	
Metal Complexes	Solid	Dispersed	Solid	Dispersed	Solid	Dispersed
$[Ni(phen)_3]SO_4$	114	114	120	144	225	265
$[Ni(phen)_3]Cl_2$	114	114	125	135	170	220
$[Ni(bpy)_3]SO_4$	114	114	120	138	135	190
$[Ni(bpy)_3]Cl_2$	114	114	115	136	125	170

Note. Values are in Meq/100 g of clay.

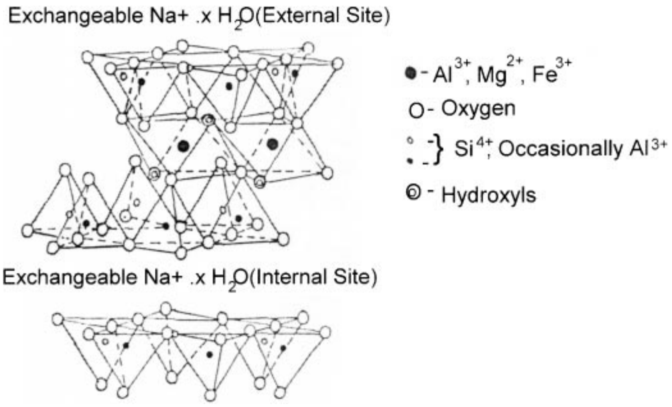

FIG. 3. Layered structure of Na–montmorillonite clay with outer and inner ion-exchange sites.

Na–montmorillonite shows interlayer swelling upon treatment with water and ultimately results in delamination of the platelets. Therefore, the ratio of internal and external sites (Fig. 3) depends upon the aggregation number, which in turn depends upon the dispersion of the clay (10a, 10c, 14). The layers of such clay are held together by van der Waals forces as a face-to-face aggregate and may be expressed as

$$V_A = -(A/48\pi)\{1/d^2 + 1/(d+\Delta)^2 - 2/(d+\Delta/2)^2\}, \quad [1]$$

where V_A is van der Waals energy (erg cm^{-1}), d is the half-distance between the plates, Δ is the unit layer thickness (9.6 Å), and A is a constant having value $\sim 10^{-12}$. Due to swelling, V_A decreases and ultimately delaminates. Since, V_A is weak, comparatively little energy is required to intercalate into the layers by some suitable species. As the layers move apart from each other, the attractive energy decreases and therefore the energy required for expansion will be less (6b). At layer separation of about 6.5 Å, the value of V_A is only 0.6 mJ/m^2. Therefore, the intercalation reaction of air-dried (at room temperature) clay having a basal spacing (d_{001}) of about 12.5 Å with cationic species like $[Ni(phen)_3]^{2+}$ or $[Ni(bpy)_3]^{2+}$ does not involve much energy (29). Recently, solid–solid intercalation reactions between Na–montmorillonite (dried at 120°C and showing interlayer separation of 2.9 Å) and the $[Co(phen)_3]^{2+}$ complex has been reported to occur (9a). For such an exchange reaction at least a minimum quantity of liquid-state, i.e., interlamellar, hydrated phase is required for ionic transport and this may indicate that Na–montmorillonite dried at 300°C does not intercalate with the metal complex (9a) because of the absence of the interlamellar liquid phase. The intersalation reaction exhibited by predispersed clay is more prominent than that of undispersed clay (Table 2). The basal spacing (d_{001}) of such an intersalated product is about 29 ± 1 Å, which is almost equivalent to the summation of the single layer thickness (9.6 Å) of the clay platelet, the diameter (∼16 Å) of the two cations of the metal complex, and the diameter of SO_4^{2-} (∼4 Å) and thus indicates the formation of a bilayer cationic metal complex within the interlamellar spacings (13, 15). Moreover, if the intersalated compounds are not washed thoroughly, basal spacing (d_{001}) above 30 Å is obtained and, in the case of $[Ni(phen)_3]SO_4$–montmorillonite, the value is above 32 Å (Fig. 4) indicating, the formation of a pseudo-trilayer metal complex in the interlamellar spacing. This is perhaps the first report of such an intersalated compound. Therefore, bilayer or pseudo-trilayer formation of the complexes in the interlamellar spacing does not only depend upon the amount of metal complex adsorbed by the intersalation reaction but also depends upon the mode of clay pretreatment.

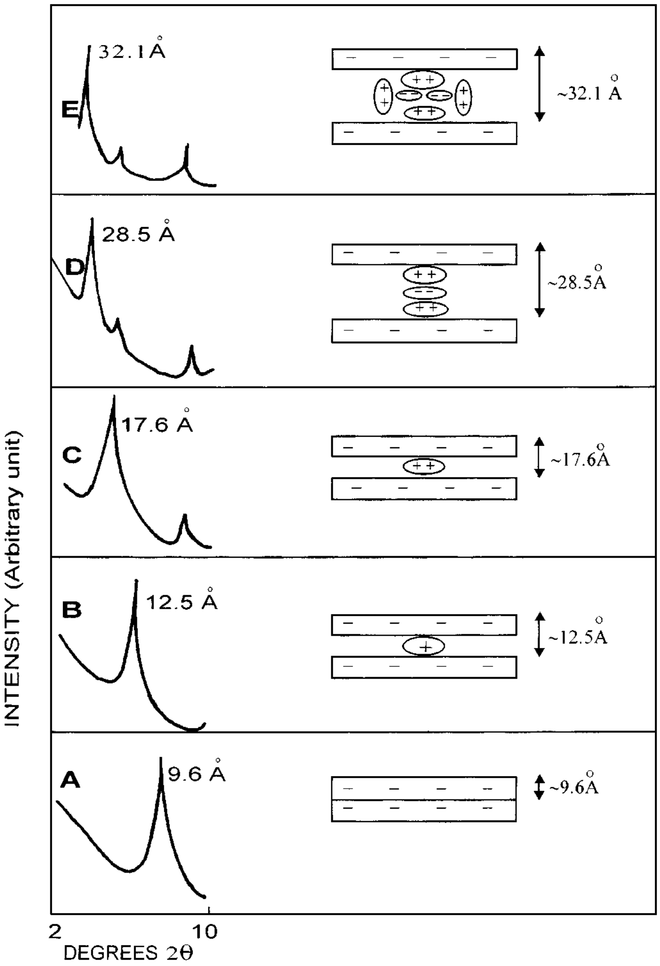

FIG. 4. X-ray diffraction patterns and schematic representation of (A) collapsed Na–montmorillonite, (B) dried (room temperature) Na–montmorillonite, (C) intercalated $[Ni(phen)_3]$–montmorillonite, and (D and E) intersalated products of $[Ni(phen)_3]SO_4$ with Na–montmorillonite.

TABLE 3

Amount of $[Ni(phen)_3]SO_4$ Adsorbed on Na–Mont under Different Autoclaving Conditions

Temperature (°C)	Pressure (atm)	$[Ni(phen)_3]SO_4$ adsorbed (Meq/100 g clay)
80	0.5	147
90	0.7	157
100	1.0	160
110	1.4	165
120	2.0	176

The exchange reaction of Na–montmorillonite clay with divalent metal ions, from the thermodynamic principle, leads to an increase in entropy and is an endothermic process (29). The van't Hoff equation [2] derived from thermodynamics indicates that in an endothermic reaction (where H_o is positive) the equilibrium shifts toward adsorption as the temperature rises. Therefore, an increase in temperature favors the adsorption

$$\frac{d\ln K}{dT} = \frac{H_o}{RT^2}, \qquad [2]$$

(where K = equilibrium constant of exchange, H_o = enthalpy, R = constant, T = absolute temperature) reaction and it is evident that the stirring condition at room temperature in the present study shows the lowest adsorption compared to conditions at higher temperatures, such as refluxing, autoclaving, and ultrasonication (in the ultrasonic system, although the overall temperature of the reaction mass rises slightly, tremendous high temperature develops momentarily in the internal mass). In support of the above, the adsorption reaction of $[Ni(phen)_3]SO_4$ on Na–mont at different temperatures under autoclaving conditions was carried out where the amount of adsorption was found to increase with increasing reaction temperature (Table 3). Again, the ultrasonic condition not only favors the adsorption reaction by raising the local temperature, but also may enhance the reaction by delamination and cracking the particles into smaller sizes, thereby increasing the reactive surface area and improving mass transport. This is revealed by the enhancement of surface area from 93.8 m^2/g for Na–mont before sonication to 119.3 m^2/g after sonication.

In a dehydrated system, the silicate layers of the clay are in a fully collapsed state (Fig. 4A) and, therefore, adsorption takes place predominantly on the external surface of the layers (2). But in a partly dehydrated system where the layers of the clays are already slightly separated, the intercalation reaction with the appropriate species occurs. It has been reported (24) that hydrated metal ions in the interlamellar spacing possesss ionic mobility similar to that found in the bulk of the solution. This ionic mobility may prompt the cation exchange reaction and help to expand the layers. Therefore, intercalation or intersalation reactions of the metal complexes with the clay surface take place in the opposite fashion when the clays are in highly

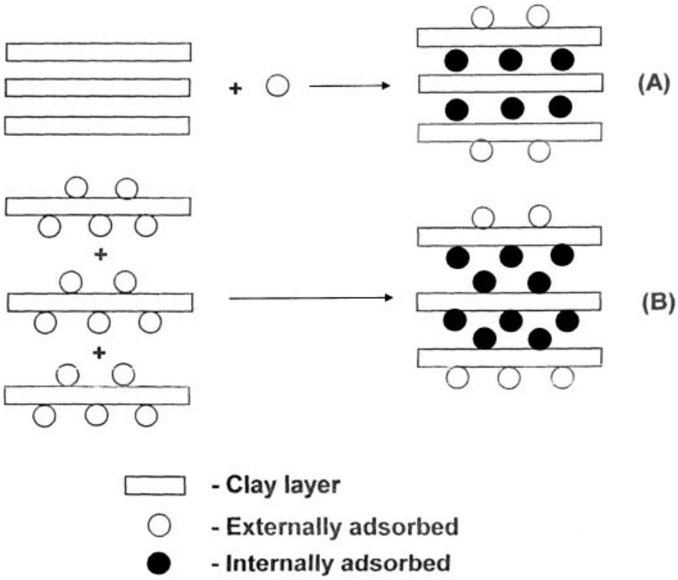

FIG. 5. Monolayer and bilayer formation of metal complexes in the interlamellar spacing (A) from aggregated clay and (B) from dispersed clay.

aggregated (room temperature dried) and dispersed forms. Figure 5 depicts the state of the reactions i.e., in the aggregated form, work is required to prop open the layers to accommodate the bulky metal complexes into the interlamellar space, while in the case of predispersed clay, the platelets which are already adsorbed with the metal complex laminate to form a layered structure. Therefore, the formation of a monolayer, bilayer, or pseudo-trilayer metal complex in the interlamellar space could be easily explained from Fig. 5.

The d_{001} reflection near 17.86 Å of the monolayered intersalated product obtained from $[Ni(phen)_3]SO_4$ and clay (dried) is stable up to 350°C, but at 450°C it shifts to 12.81 Å, indicating the decomposition of the interlamellar metal complexes (Fig. 6). Upon further heating up to 550°C, the $d_{(001)}$ reflection shows a value of 9.72 Å, confirming a completely collapsed structure of montmorillonite (Fig. 6E). The d_{001} reflection of the bilayered compound at 28.51 Å (Fig. 7) is stable up to 250°C and thereafter changes to a monolayer, showing a d_{001} reflection at 17.68 Å, which is stable up to 450°C. Upon heating to 550°C, the basal spacing (d_{001}) is found to be 12.91 Å, which comes down to 10.05 Å upon further heating at 650°C. This clearly reflects that the stability of monolayer derived from the bilayer is higher than that obtained directly from the metal complex and dried clay. This extra thermal stability is assumed to be due to the presence of a higher amount of metal complex salt in the interlayer space. Again, the d_{001} reflection of the bilayer metal complex at 650°C (Fig. 7) shows a slightly higher value than that of monolayer compound at 550°C (Fig. 6), indicating that, in the former, residue of decomposed products still persists in the inter layer space. It may be mentioned here that the thermal stability of low-loaded metal complexes ($<$0.5 CEC) is only upto 250°C; beyond that basal spacing (d_{001}) comes down to 12.5 Å from 17.5 Å. This clearly indicates that the amount of metal complexes loaded into the interlayer space has a direct contribution to thermal stability.

Thermal (DTA and TGA) analyses of the intercalated and intersalated ($[Ni(phen)_3]SO_4$–mont) products are shown in Fig. 8. The TGA curve (Fig. 8A) of the 1 CEC Eqv intercalated product obtained from the dry clay shows a mass loss of about 7.3% up to a temperature of about 100°C, which is attributed to moisture loss. There is a gradual mass loss of about 19% in the temperature range 350 to 550°C, which corresponds to the decompostion and partial oxidation of the interlamellar metal complex. The corresponding exothermic DTA peak is observed at 530°C. This observation is corroborated by the static thermal characteristics (Fig. 6). In the temperature range 550 to 650°C, the mass loss of about 5.3% is attributed to oxidation of the left-out carbonaceous materials from the organic moiety. The corresponding exothermic DTA peak occurs at 625°C. The bilayered 2.9 CEC Eqv adsorbed product obtained from the dispersed clay shows

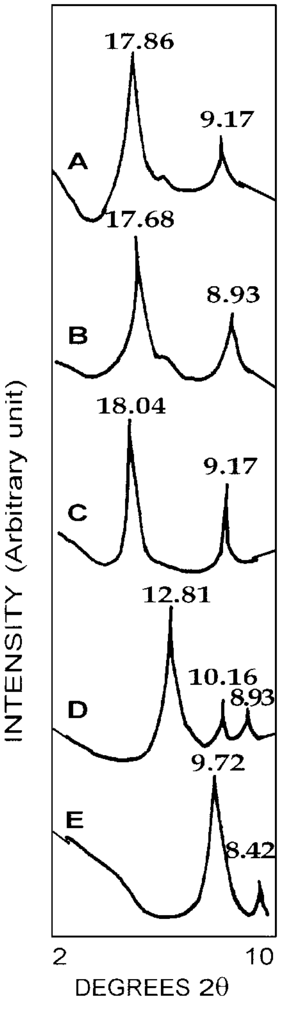

FIG. 6. X-ray diffraction patterns of $[Ni(phen)_3]$–montmorillonite monolayered compound treated at (A) room temperature, (B) 250°C, (C) 350°C, (D) 450°C, and (E) 550°C (each sample was heated for 1 h).

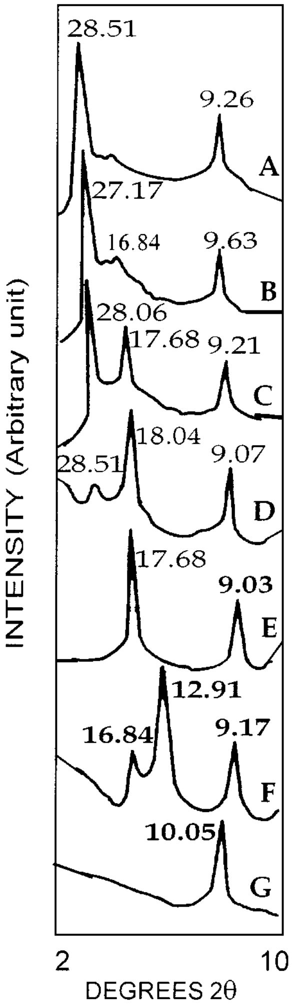

FIG. 7. X-ray diffraction patterns of $[Ni(phen)_3]SO_4$–montmorillonite bilayer compounds at (A) room temperature; (B) 100°C, (C) 250°C, (D) 350°C, (E) 450°C, (F) 550°C, and (G) 650°C (each sample was heated for 1 h).

(Fig. 8B) a mass loss of about 9% up to 120°C, which is attributable to moisture loss. There is a gradual mass loss of about 29.2% over the temperature range 300 to 650°C, which is due to decomposition and oxidation of the organic moiety of the metal complex. The corresponding DTA peak appears at 540°C, which indicates a higher thermal stability than that of the monolayered intersalated product. This observation is also corroborated by the static thermal characteristics (Fig. 7).

As a typical example, the characteristic ir bands of $[Ni(phen)_3]SO_4$ at 1518, 1425, 1340, 848, 725, and 618 cm^{-1} are found to shift slightly toward the higher range in intercalated or intersalated products (Fig. 9). The monolayered intersalated product ($d_{001} \sim 17.5$ Å), prepared from the interaction of metal complexes with solid Na–montmorillonite, shows characteristics ir bands up to about 350°C. The intensity of the bands at 450°C is considerably reduced and thereafter completely vanishes at 550°C, indicating the decomposition of the metal complex. This observation has been corroborated by the XRD reflections (Fig. 6E) of the same compound heated at 550°C. The metal complex $[Ni(phen)_3]Cl_2$ shows a similar result. The characteristic ir bands of $[Ni(bpy)_3]SO_4$ at 1595, 1465, 1314, and 728 cm^{-1} are found to shift to higher values of 1610, 1490, 1360, and 750 cm^{-1}, respectively, in the intercalated or intersalated products. The thermal stability of the products is similar to that of $[Ni(phen)_3]SO_4$–mont products. When the loading of the metal complex is in the range 0.1–0.5 of CEC, the thermal stability is less compared to that with higher loading. This may be attributed to higher pillaring action.

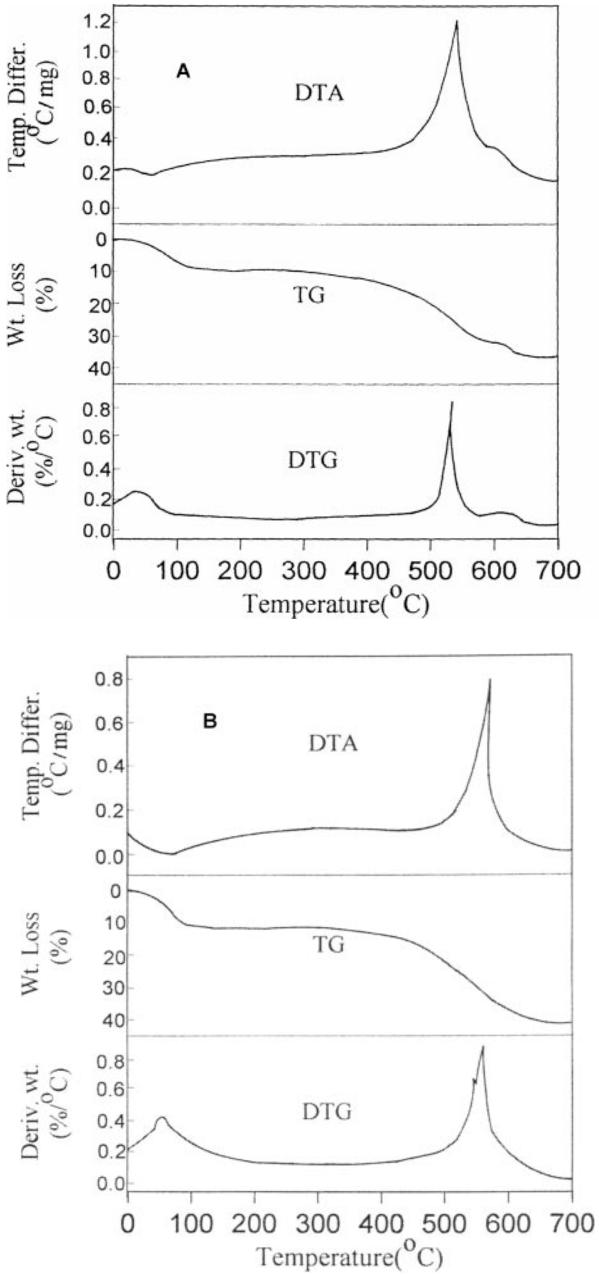

FIG. 8. Thermal analyses curves (DTA, TGA, and DTG) of the intercalated (A) and intersalated (B) $[Ni(phen)_3]SO_4$–mont products.

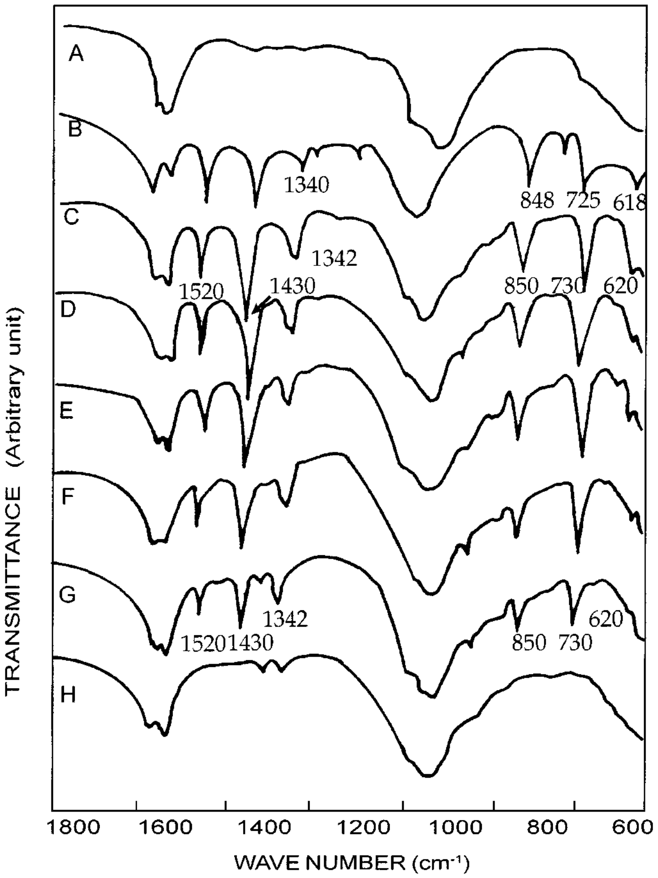

FIG. 9. Infrared spectra of (A) Na–montmorillonite, and (B) $[Ni(phen)_3]SO_4$, $[Ni(phen)_3]SO_4$–montmorillonite bilayered compounds treated at (C) room temperature dried, (D) 100°C, (E) 250°C, (F) 350°, (G) 450°, and (H) 550°C (each sample was heated for 1 h).

The surface area of the metal-complex–mont composites, as determined by N_2 adsorption at 77 K after degassing at 120°C for 2 h and calculated using the BET equation, is shown in Table 4. Neat Na–mont shows the highest surface area, i.e., 93.8 m^2/g. Up to the CEC, as the loading of the metal complexes in the intercalated products increases, the surface areas decrease accordingly. But in intersalated products, the magnitude of the surface area is extremely low, which may be attributed to filling up of the empty space in the interlamellar region by the intersalated salt, or it may be due to the formation of an impermeable layer for diffusion of N_2 into the interlayer region (27).

TABLE 4
Surface Area Data of Some Samples

Sample no.	Sample	Surface area (m^2/g)
1	Na–Mont	93.8
2	0.1 CEC $[Ni(phen)_3]$–Mont	65.8
3	0.5 CEC $[Ni(phen)_3]$–Mont	26.9
4	1.0 CEC $[Ni(phen)_3]$–Mont	14.9
5	2.3 CEC $[Ni(phen)_3]$–Mont	1.73
6	0.1 CEC $[Ni(bpy)_3]$–Mont	44.2
7	0.5 CEC $[Ni(bpy)_3]$–Mont	40.0
8	1.0 CEC $[Ni(bpy)_3]$–Mont	32.7
9	1.6 CEC $[Ni(bpy)_3]$–Mont	6.24

SUMMARY

Intersalation reactions between $[Ni(phen)_3]SO_4$ or $[Ni(phen)_3]Cl_2$ or $[Ni(bpy)_3]SO_4$ or $[Ni(bpy)_3]Cl_2$ and Na–montmorillonite carried out under (i) ultrasound irradiation; (ii) refluxing; (iii) autoclaving, and (iv) vigorous stirring are found to be complete within about 30 min. Under ultrasonic conditions, the highest amount of metal complex adsorption occurs. The phen-containing metal complex gives a higher adsorption than that containing bpy. Highly aggregated and dispersed clay gives mono- ($d_{001} \sim 17.5$ Å) and bilayered ($d_{001} \sim 28.5$ Å) or pseudo-trilayered ($d_{001} \sim 32$ Å) intersalated products, respectively. Adsorption of metal complexes up to about three times the cation exchange capacity of the clay is observed. Dispersed clay always adsorbs a higher quantity than undispersed clay. The surface areas of the intersalated products are extremely low. Bilayered intersalated products are thermally stable up to about 250°C; beyond this temperature they convert to monolayered products which are stable up to about 450°C. Intersalated products show higher thermal stability than unintersalated ones.

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