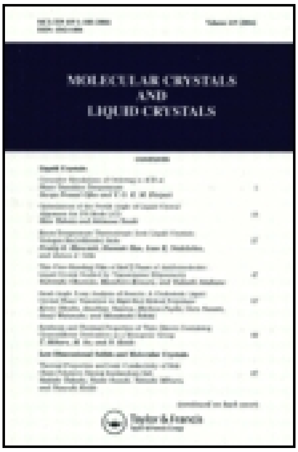

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

To cite this article: Wataru Fujita & Kunio Awaga (1995): Intercalation of Pyridinium Nitronyl Nitroxides into the Saponite Clay Interlayers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 271:1, 123-128

To link to this article: http://dx.doi.org/10.1080/10587259508034045

Mol. Cryst. Liq. Cryst., 1995, Vol. 271, pp. 123–128
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INTERCALATION OF PYRIDINIUM NITRONYL NITROXIDES INTO THE SAPONITE CLAY INTERLAYERS

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Abstract The *N*-alkylpyridinium nitronyl nitroxide cations were intercalated into saponite clay ($Na_{0.46}[Si_{3.54}Al_{0.46}Mg_3O_{10}(OH)_2]\cdot nH_2O$) by means of the cation exchange. Up to 70 % of the sodium ions were replaced by the organic radicals. The organic radical-saponite nanocomposites were found to show Curie paramagnetic behavior.

INTRODUCTION

In recent years, considerable effort has been devoted to investigation of organic radicals exhibiting ferromagnetic properties.[1] It is reported that essential conditions for the intermolecular ferromagnetic coupling are (1) large spin polarization and (2) small SOMO-SOMO overlap, and large SOMO-NHOMO and/or SOMO-NLUMO overlaps in the nearest-neighbor molecular arrangement.[2] The intermolecular magnetic interaction would depend seriously on the intermolecular arrangement. Therefore it is an interesting work to put organic radicals into different environments from those in their bulk crystals, given in hosts, in interlayers, in clusters, on surfaces, etc., and to examine the magnetic properties.

A clay mineral, saponite ($Na_x[Si_{4-x}Al_xMg_3O_{10}(OH)_2]\cdot nH_2O$), has a lamellar structure consisting of a two dimensional array of the mineral lattice, shown in Figure 1.[3] The octahedral magnesia layer is sandwiched between the two silica layers. The layers charge negatively because of Al^{3+} in substitution for Si^{4+} in the tetrahedral sites. The sodium ions are located in the interlayer together with the water molecules, compensating the negative charges in the layer. The interlayer is bound by a weak van der Waals interaction, in contrast to the strong covalent bonds connecting the intralayer, so that various guest molecules and ions are easily inserted into the van der Waals gap. If the guest molecule forms an ensemble with a different intermolecular arrangement from that in the bulk, new properties will appear in the host. There are precedents for organic radical insertion into inorganic interlayers; DPPH-saponite,[4] DPPH-montmorillonite,[4] and TTF^+-MPS_3 (M=Fe, Mn and Cd),[5] although the amount

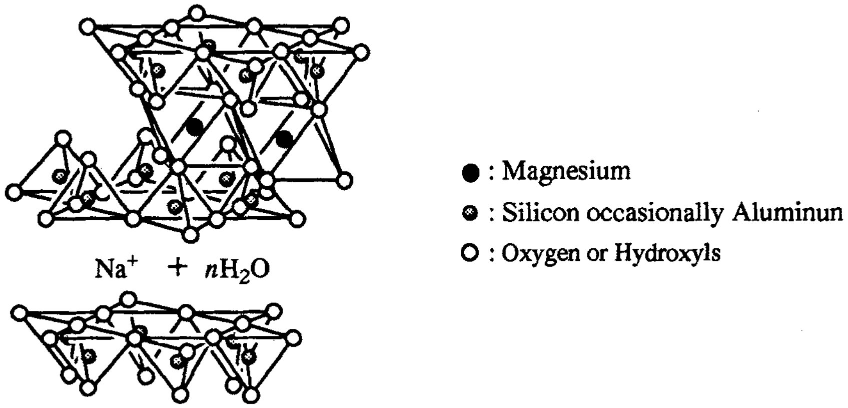
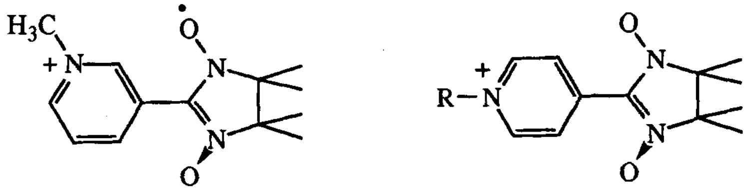


FIGURE 1 Structure of saponite clay.



1^+ R= CH_3 (2^+), C_2H_5 (3^+) and n-C_4H_9 (4^+)

FIGURE 2 Structure of the intercalated radicals.

of the DPPH is very small in the clays, and there is no quantitative magnetic measurement revealing the magnetic interaction of TTF^+ in MPS_3. In this paper we report the intercalation of *N*-alkylpyridinium nitronyl nitroxides (See Figure 2) into the saponite interlayer. We also describe their magnetic properties.

EXPERIMENTS

Saponite clay ($Na_{0.46}[Si_{3.54}Al_{0.46}Mg_3O_{10}(OH)_2]{\bullet}nH_2O$) was purchased from Kunimine Chemical Co. Ltd., whose cation exchange capacity (CEC) was 100.43 mequiv/100 g of the clay. The organic radicals were prepared according to the reported methods.[6,7] The intercalation was carried out, stirring the aqueous solution of the clay and the organic radical for 3 hours. The precipitate was filtrated with a membrane filter (Toyo Roshi Ltd., 5 mm), and dried under vacuum at room temperature for a day. The amount of the inserted guest was estimated from the difference in the UV absorption intensity (Jasco

Co. Ltd. V-550) between the original solution and the filtrate. The interlayer distances of the parent sodium-saponite and the saturated intercalates were determined by powder X-ray diffraction (Rigaku Denki Co. Ltd. RAD-C System). The static magnetic susceptibility was measured in a field of 1 Tesra by using a Faraday balance. The details of the apparatus were described previously.[8]

RESULTS AND DISCUSSION

Figure 3 shows the intercalation curves for the organic radicals, where the horizontal axis is defined as the ratio of the radical in the original solution to the CEC of the saponite and the vertical axis is done as the ratio of the inserted radical to the CEC. The four curves show similar dependence: the intercalate increases exponentially with increasing the radical concentration, and, after passing through an inflection point, it reaches the saturation of *ca.* 70 % of the CEC. The interlayer distances of the parent sodium-saponite and the saturated intercalates are shown in Table I, where calculated molecular heights of the nitroxides and the diameter of a sodium ion are also listed. The interlayer distance of the sodium-saponite is more than two times longer than the sodium diameter, presumably because the sodium ions are hydrated in the layer. On the other hand, the interlayer distances of 1^+ and 2^+ approximately correspond to their molecular heights. The effect of hydration on the size of organic molecules could be smaller than that on the sodium ion. Therefore, the molecular axes of 1^+ and 2^+ are thought to be

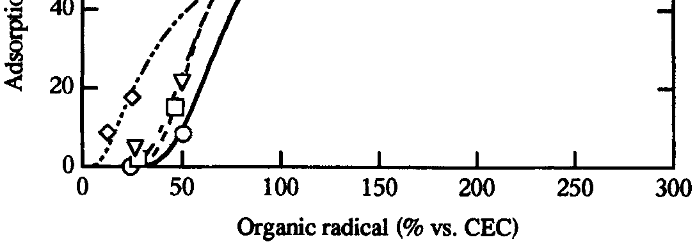


FIGURE 3 Intercalation curves of 1^+ (—○—), 2^+ (- - -□- - -), 3^+ (- —▽— -) and 4^+ (-···◇···-). The curves are guides for eyes.

TABLE I Interlayer distances of the parent and intercalated saponite clays.

Interlayer Cation	Interlayer Distances (Å)	Molecular Height [a] or Ion Diameter (Å)
Na^+	5.8	2.0
1^+	9.7	9.4
2^+	9.0	10.2
3^+	9.0	12.1
4^+	8.6	14.2

a) Molecular heights of the radicals were estimated from PM3 molecular orbital calculations.[9]

aligned nearly perpendicular to the layer. The interlayer distances of 3^+ and 4^+ are shorter than their molecular heights, suggesting a tilted structure. This could be due to the fact that the bulky alkyl group protects the positive charge on the pyridinium ring from the negative charge in the mineral layer.

Temperature dependence of the magnetic susceptibilities of the parent saponite and the saturated intercalates were measured in the temperature range of 3-280 K. Paramagnetic susceptibilities, χ_p, were obtained by compensating the diamagnetic susceptibilities that were evaluated from the experimental data by assuming that the paramagnetic part follows the Curie law above 200 K. Figure 4 shows the plots of $\chi_p T$ *vs*. *T*. The parent sodium-saponite which is intrinsically diamagnetic, is found to include a small Curie paramagnetic component. The obtained Curie constant, C=6.75x10^{-7} emu K g^{-1}, is so small that it could be due to transition metal-ion impurities. The anomaly around 65 K can be assigned to the effect of the oxygen adsorbed on the sample surface and/or in the interlayers.[10] The temperature dependence of χ_p of the intercalates also follow the Curie law, and also show anomalies around 65 K. The Curie constants are calculated to be C=2.12x10^{-4} emu K g^{-1} for the 1^+-saponite, 2.17x10^{-4} emu K g^{-1} for the 2^+-saponite, 2.27x10^{-4} emu K g^{-1} for the 3^+-saponite and 2.22x10^{-4} emu K g^{-1} for the 4^+-saponite that are two orders of magnitude larger than that of the parent saponite. The Curie constants agree with the theoretical value of C=2.10x10^{-4} emu K g^{-1}, assuming a reasonable chemical formula, $Na_{0.14}(\text{Organic Radical})_{0.32}[Si_{3.54}\ Al_{0.46}Mg_3O_{10}(OH)_2]\cdot 10H_2O$. The anomalies prevent us from calculating the Weiss constants exactly, but the temperature dependence above 100 K suggests that their absolute values are less than 5 K. These organic cation radicals stably survive still in the interlayers, although the magnetic interaction observed in their iodide salts disappear.[11] Assuming a homogeneous distribution of the cation and complete exchange between the organic radical cation and the sodium ion, the average distance between the inserted is expected

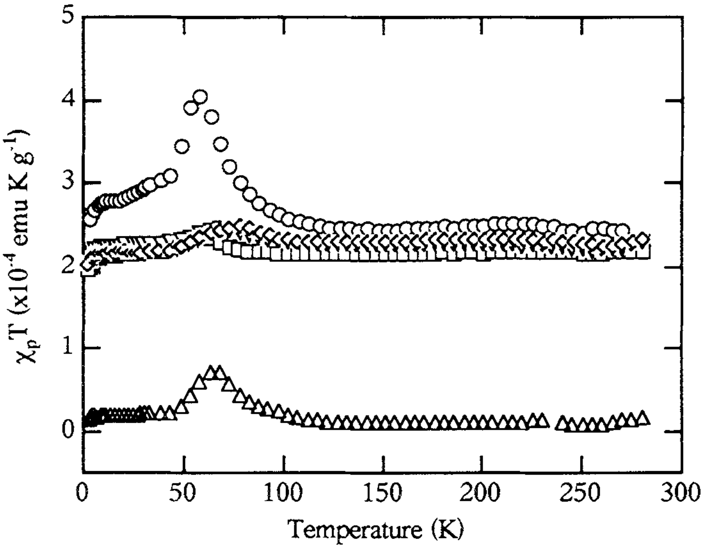


FIGURE 3 Temperature dependence of χ_p of the parent saponite (△) and the saturated intercalates with 1^+ (○), 2^+ (□), 3^+ (▽) and 4^+ (◇).

to be *ca.* 5.5 Å.[12] The observed weak magnetic interaction can be understood in terms of the long distance between the organic guest radicals. In the other words, the magnetic behaviors suggest the dominance of the host-guest interaction and the homogeneous distribution of the cation exchange sites in the saponite interlayer.

CONCLUSION

We have carried out the intercalation of the nitronyl nitroxide cations into the saponite clay and the magnetic measurements. In this work, *ca.* 70 % of the sodium ions in the original saponite are replaced by the organic radical cations without chemical decomposition. The magnetic interactions of the organic radicals in their iodide salts disappear, and the intercalates show Curie paramagnetism.

ACKNOWLEDGMENT

This work was supported by the Grant-in-aid for Scientific Research from the Ministry of Education, Science, and Culture, Japanese government. Support from New Energy and Industrial Technology Development Organization (NEDO) is also acknowledged.

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