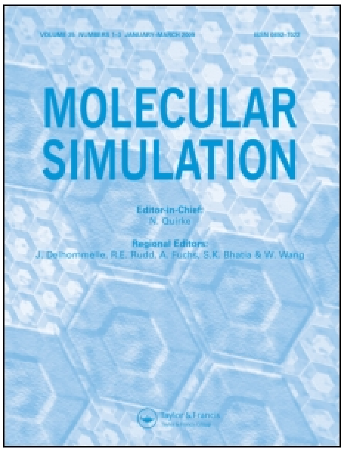

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Molecular Dynamics Simulations of The Swelling of Terephthalate Containing Anionic Clays

Samuel J. Williams[a]; Peter V. Coveney[a]; William Jones[b]
[a] Schlumberger Cambridge Research Ltd., Cambridge, UK [b] Department of Chemistry, Cambridge University, Cambridge, UK

To cite this Article Williams, Samuel J. , Coveney, Peter V. and Jones, William(1999) 'Molecular Dynamics Simulations of The Swelling of Terephthalate Containing Anionic Clays', Molecular Simulation, 21: 4, 183 — 189

To link to this Article: DOI: 10.1080/08927029908022060

URL: http://dx.doi.org/10.1080/08927029908022060

Molecular Simulation, 1999, Vol. 21, pp. 183–189
Reprints available directly from the publisher
Photocopying permitted by license only

MOLECULAR DYNAMICS SIMULATIONS OF THE SWELLING OF TEREPHTHALATE CONTAINING ANIONIC CLAYS

SAMUEL J. WILLIAMS[a], PETER V. COVENEY[a,]* and WILLIAM JONES[b,]*

[a] *Schlumberger Cambridge Research Ltd., High Cross, Madingley Road, Cambridge CB3 0EL, UK;*
[b] *Department of Chemistry, Cambridge University, Lensfield Road, Cambridge CB2 1EW, UK*

(Received April 1998; accepted May 1998)

We report on molecular simulations of the swelling of terephthalate-containing anionic clays. We find good agreement with experimentally derived interlayer spacings, and models for the structure and dynamics of the interlayer water. We predict a swelling profile which suggests that at high water content a sharp increase in interlayer spacing will occur. The corresponding swelling curve for methanol incorporation, however, indicates a more continuous expansion.

Keywords: Molecular dynamics; LDHs; anionic clay

INTRODUCTION

The general formula of an anionic clay (hydrotalcite) composed of a mixture of magnesium and aluminum cations may be written as $[\mathrm{Mg}^{2+}_{1-x}\mathrm{Al}^{3+}_{x}(\mathrm{OH})_2]$ $[x/n\mathrm{A}^{n-}m\mathrm{H_2O}]$ where A^{n-} is the charge-balancing anion and $x = \mathrm{Al}^{3+}/(\mathrm{Mg}^{2+} + \mathrm{Al}^{3+})$. The ratio of $\mathrm{Mg}^{2+}:\mathrm{Al}^{3+}$ is typically between 2 and 3 [1]. Experimental measurements have shown that the position and orientation of the anions, as well as the amount of water present, is important in determining the properties of such a clay [2–4].

---

*Corresponding authors.

Whilst a range of computational techniques have been useful in the study of the cationic clay minerals [5, 6], little work on anionic clays has been reported [2, 7, 8].

Previous simulation work by us [7] was carried out using an experimentally-derived hydrotalcite structure in which the Mg:Al ratio was 3:1 [9]. The work reported here uses a similar structure but with a higher Al^{3+} content, such that the Mg:Al ratio is 2:1. In particular, whilst the role of water is known to be important in anionic clays its full significance has not, to date, been probed either by experiment or simulation. Earlier work by us was restricted to a few points on the water uptake curve and did not investigate the properties of the incorporated water itself [7]. The primary aim of the work reported here is to study how the properties of terephthalate-containing 2:1 anionic clay will be affected by changes in the water content. Comparisons to experiment [2, 4, 3], previous molecular simulations [2, 7] and cationic clays [5, 6] are made.

SIMULATION METHODS

The model and interaction parameters are as described in our previous paper [7]. All molecular dynamics (MD) simulations were performed at 300 K with specific numbers of water molecules present within the interlayer gallery. The initial model for each of these simulations was built with a layer repeat of 14.40 Å and the terephthalate anions randomly positioned in an orientation approximately perpendicular to the layers, approximating that observed experimentally.* A total of 6 anions (3 per interlayer) were required to ensure electroneutrality, and the appropriate number of water or methanol molecules were randomly positioned around the anions.

The total simulation time was generally 20 ps which gave equilibrium values for the interlayer spacings over the last half of the MD run, as judged by these spacings remaining essentially constant. The simulation properties were averaged over this equilibrated region to provide some statistical data. The results of the MD calculations are shown in Table I, where the number of water molecules per supercell; the average interlayer spacing calculated (*d* avg); the minimum and maximum interlayer spacings observed are given. The results are presented graphically in Figure 1 where the error bars represent the fluctuations about the average interlayer spacing (two standard deviations in each direction).

---

* The simulation cell was made up with 6 × 3 × 2 unit cells. This was found to be the optimum cell size which gave consistently accurate results without unreasonably long processing times.

TABLE I Results of terephthalate intercalated anionic clay molecular dynamics simulations at 300 K with varying water and methanol contents

	Water					*Methanol*	
Content molecules	*d avg Å*	*d min Å*	*d max Å*	*d SD Å*	*Pack ratio*	*d final Å*	*Pack ratio*
0	12.09	11.69	12.49	0.24	0.71	12.11	0.71
4	11.28	10.90	11.60	0.25	0.78	12.48	0.74
8	12.60	12.37	12.90	0.17	0.74	12.49	0.80
12	12.06	11.59	12.57	0.21	0.80	13.17	0.81
16	13.17	13.01	13.32	0.08	0.85	13.60	0.80
20	12.61	12.34	12.81	0.14	0.82	13.71	0.85
24	13.04	12.83	13.38	0.16	0.81	14.08	0.87
28	13.33	13.08	13.57	0.14	0.80	14.31	0.88
32	13.51	13.29	13.72	0.15	0.86	14.70	0.89
36	13.69	13.48	13.84	0.10	0.84	15.58	0.87
40	14.07	13.91	14.25	0.09	0.81	17.15	0.85
44	13.87	13.67	14.02	0.08	0.88	34.54	0.71
48	14.01	13.88	14.12	0.07	0.87	20.60	0.67
52	14.22	14.03	14.52	0.13	0.88	28.51	0.60
56	14.03	13.93	14.19	0.06	0.89	45.60	0.68
60	15.56	15.42	15.66	0.06	0.85	81.93	0.68
64	16.06	15.71	16.31	0.14	0.86	–	–

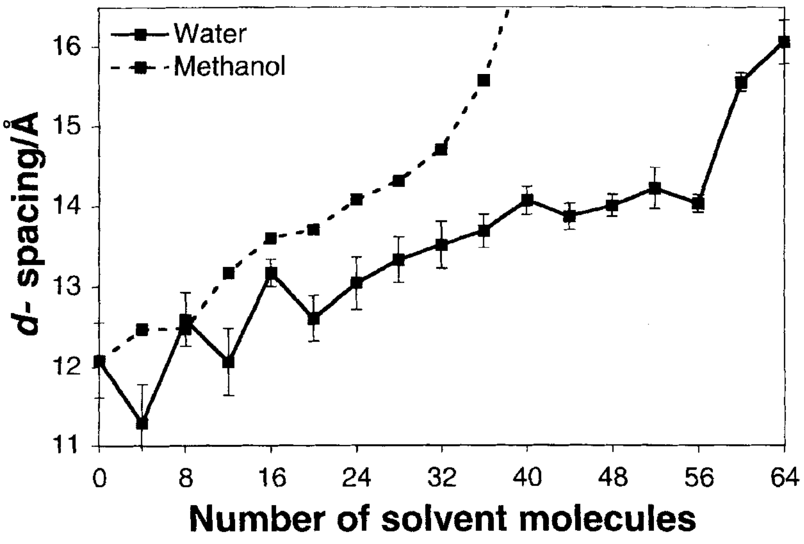

FIGURE 1 Graph showing variation of interlayer spacing with water and methanol content per simulation cell for terephthalate intercalated anionic clay. A plateau is evident between 40 and 56 water molecules at around the experimental value of interlayer spacing at 14.0 Å.

RESULTS AND DISCUSSION

Examination of the properties of the interlayer water was carried out using data extracted from the trajectory file of a much longer (200 ps) MD run containing 44 water molecules, since this system corresponds most closely to existing experimental samples in terms of water content and interlayer spacing;** the increased length of the simulation improves the statistics and enables us to extract a meaningful water self-diffusion coefficient. The water forms a bilayer comprising sheets adjacent to the hydroxide surfaces. The water (O—O) radial distribution function (RDF) was calculated using coordinate data from the last 190 ps of the run (after 10 ps of equilibration) and shows some similarities to that for bulk water. A large, sharp peak at 2.9 Å represents the first coordination shell and a second peak at 5.6 Å is due to the second coordination shell, both within individual sheets. There is also a third, broad peak at about 7.5 Å which corresponds to sheet–sheet water distances. Although some of the water molecules do spend time in the centre of the gallery (a relatively hydrophobic region), there is no evidence for the formation of a trilayer (which would be manifested by a peak in the RDF at about 3.8 Å). The water self-diffusion coefficient was calculated from a linear fit of the mean squared displacement computed. The self-diffusion coefficient obtained ($5.90 \times 10^{-7}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$) compares well to experimental data (between $2.47 \times 10^{-7}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ and $4.60 \times 10^{-7}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$(between 50–150°C)) [10].

As expected, there is a general trend for the layer spacing to increase with increasing water content; the fluctuations also decrease (see Fig. 1). Between 0 and 20 water molecules there is a significant oscillation in the average interlayer spacings and also large fluctuations. The latter may be simply explained by there being few molecules in the interlayer, and thus greater scope for different molecular arrangements of similar energy. The large variation in interlayer spacings between simulations of different water content is not necessarily unexpected – this phenomenon is also seen in experiments and simulations on cationic clays [5, 6]. Approaching the range 40–56 water molecules, a levelling-off in interlayer spacing is observed as is the development of a plateau region at around the experimentally reported value of 14.0 Å [4, 3]. The fluctuations are particularly small in this region, suggesting the system at around this level of water content is 'stable'.

In particular we note that all of the simulations up to and including 56 water molecules show the terephthalate anions to be bridging the interlayer

---

** Experimental thermal gravimetric analysis of a 2 : 1 Mg/Al terephthalate clay gives a value for the water content of 20 wt%, approximating to 44 water molecules in our simulations.

region by hydrogen bonding to hydroxyl groups on each surface-in agreement with experiment. Above 60 water molecules, however, each terephthalate anion is detached from one layer and water molecules insert themselves between the carboxylates and the hydroxide layer; there is a concomitant increase in interlayer spacing to about 15.5 Å (see Fig. 2).

The fluctuation in calculated interlayer spacing for 52 molecules is relatively large compared to that of its neighbours. In experimental studies of swelling clays, hysteresis loops are sometimes seen where the system can adopt one of two (or more) states depending on whether the experimental method involves addition or removal of water [5, 6]. It is not unreasonable

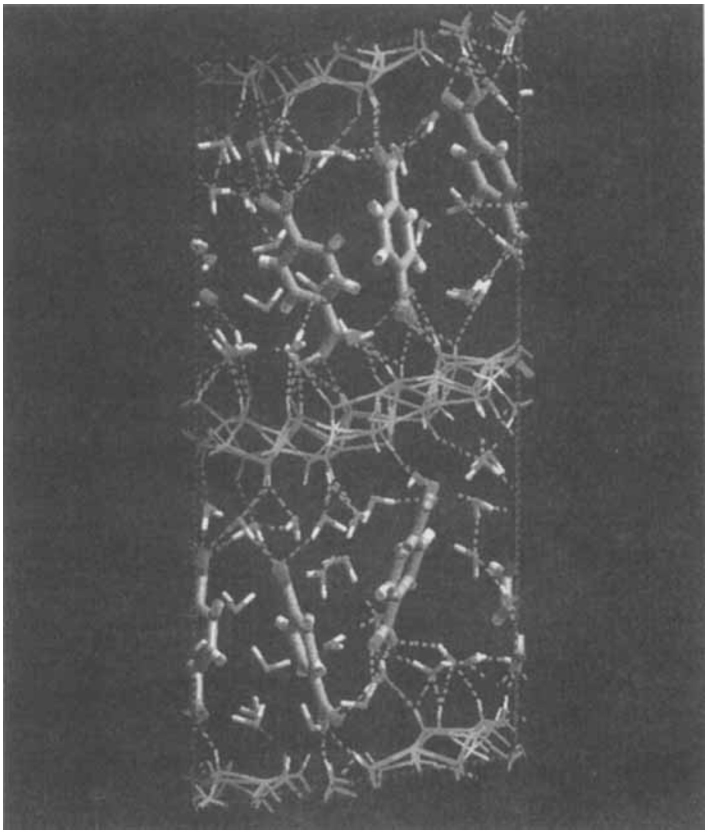

FIGURE 2 Terephthalate intercalated anionic clay with 60 water molecules per simulation cell after 20 ps of molecular dynamics at 300 K. Hydrogen bonding demonstrating the layer bridging is shown by green dashed lines, and the 3*D* periodic box is shown by blue dashed lines. The elemental colour scheme used is: Mg blue; Al yellow; O red; H white and C gray. (See Color Plate I).

to assume that a similar hysteresis effect will also be seen in anionic clays, and indeed preliminary results suggest that the 56 water system can also adopt an expanded phase at about 15.5 Å, perhaps indicative of hysteresis behaviour. The comparatively large fluctuations with 52 water molecules may be expected if at this water content the system is close to the transition between the terephthalates being attached to both surfaces being attached to one surface only. The smaller fluctuations and dual state of the 56 water system may be accounted for by its being in a region where at least two distinct and definitive profiles exist.

The corresponding swelling curve for methanol suggests a more rapid increase in interlayer spacing. The terephthalate anions become completely detached from one surface and the anionic clay expands rapidly thereafter. Calculations show that complete detachment occurs for both systems at a packing ratio of 0.89 (Tab. I).[†] This indicates that it is primarily steric packing which causes the system to expand at the point when the anions detach from the clay surface.

In computer simulations of swelling clays such as sodium montmorillonite it has been found that the sodium counter cations which normally reside close to the clay surfaces are readily solvated by the interlayer water; this substantially reduces shielding of the charged surfaces and can lead to macroscopic expansion driven by Coulombic repulsion between the sheets [5, 6]. It seems reasonable to suggest that a similar mechanism exists in the anionic clay water and methanol cases, since once the terephthalate anions cease to bridge the anionic clay layers there is little resistance to further expansion. The reason why the swelling is not observed to proceed to the same extent in the presence of water is likely to be due to a combination of effects. Firstly, water has a much higher dielectric constant than methanol which increases the electrostatic shielding between the repulsive layers, and secondly the water can form hydrogen bonds to both the carboxylate groups and the hydroxide surface, effectively extending the terephthalate bridge even after detachment has occurred.

CONCLUSIONS

Using computational methods, we predict a water swelling curve for terephthalate intercalated anionic clay with a plateau at around the

---

[†] Packing ratios were calculated as the ratio of the total van der Waals volume of the atoms to the total volume of the simulation cell.

experimental interlayer spacing value (14.0 Å with 20 wt% water content). We calculate the self-diffusion coefficient of this water at room temperature to be $5.90 \times 10^{-7}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$, which is in good agreement with experiment. At higher water contents, the swelling curve manifests a sharp 1.5 Å increase without disruption of the layer structure. We also determine that the interlayer water is distributed with a bilayer arrangement with dominant hydrogen bonding to the metal hydroxide surfaces and the terephthalate anions. We also predict that for methanol there will be no comparable plateau region in the swelling curve, and the layer spacing will rapidly expand above about 30 wt% methanol.

Acknowledgements

The authors would like to thank Molecular Simulations Inc. for facilitating access to some of the simulation software [11] and Schlumberger Cambridge Research Ltd. for financial support of this project.

References

[1] Cavani, F., Trifirò, F. and Vaccari, A. (1991). "Hydrotalcite-type anionic clays: Preparation, properties and applications", *Catalysis Today*, **11**, 173–301.

[2] Bell, I. S., Kooli, F., Jones, W. and Coveney, P. V. (1996). "Thermal Characteristics of Layered Double Hydroxide Intercalates – Comparison of Experiment and Computer Simulation", *Materials Research Society Proceedings*, **453**, 73.

[3] Vucelic, M., Moggridge, G. D. and Jones, W. (1995). "Thermal-Properties of Terephthalate-Intercalated and Benzoate-Intercalated LDHs", *J. Phys. Chem.*, **99**, 8328.

[4] Kooli, F. and Jones, W. (1996). "The Incorporation of Benzoate and Terephthalate Anions into Layered Double Hydroxides", in Synthesis of Porous Materials, Zeolites, Clays and Nanocomposites, Occelli, M. and Kessler, H., Eds., Marcel Dekker Inc., New York (USA), pp. 641–660.

[5] Boek, E. S., Coveney, P. V. and Skipper, N. T. (1995). "Monte Carlo Molecular Modelling Studies of Hydrated Li-, Na- and K-Smectites: Understanding the Role of Potassium as a Clay Swelling Inhibitor", *J. Am. Chem. Soc.*, **117**, 12608.

[6] Boek, E. S., Coveney, P. V. and Skipper, N. T. (1995). "Molecular Modelling of Clay Hydration: A study of Hysteresis Loops in the Swelling Curves of Sodium Montmorillonites", *Langmuir*, **11**, 4629.

[7] Aicken, M., Bell, I. S., Coveney, P. V. and Jones, W. (1997). "Simulation of Layered Double Hydroxide Intercalates", *Adv. Mater.*, **9**, 496.

[8] King, J. and Jones, W. (1992). "The Attempted Simulation of Layered Double Hydroxide Intercalates Through Lattice Energy Minimization", *Mol. Crys. Liq. Crys.*, **211**, 257.

[9] Allmann, R. and Jepsen, H. P. (1969). "Die Struktur des Hydrotalkits", *Neues Jahrb. Miner. Monatsh.*, **12**, 544.

[10] Kagunya, W. W. (1996). "Properties of Water Adsorbed in Anionic Clays: a Neutron Scattering Study", *J. Phys. Chem.*, **100**, 327.

[11] Molecular Simulations Inc., Cerius^2 v.2.1. and v.3.0. (1996).