ADSORPTION OF A JET FUEL ON A MODEL ORGANIC/CLAY SOIL: APPLICATION OF SMALL ANGLE NEUTRON SCATTERING

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Abstract: Small angle neutron scattering (SANS) data are reported from a system that models the contamination of a clay/organic matter soil from a fuel spillage. The soil was represented as an aqueous dispersion of the synthetic clay mineral Laponite coated with lysine, and the contaminant was a representative jet fuel, quadricyclane, mixed with the detergent cetyltrimethylammonium bromide (CTAB). The adsorbed surface coverage on the clay was estimated. It is shown that the presence of adsorbed lysine considerably enhances the subsequent adsorption of both CTAB and quadricyclane. It is demonstrated that the SANS technique can contribute to the general problem of environmental remediation and retention by probing the interactions of pollutants and clay surfaces.

Key words: clay, adsorption, SANS, fuel, groundwater

Introduction

The contamination of soils and groundwaters by hydrocarbons is an increasing problem worldwide, and there are a number of remediation techniques being applied (Song and Bartha, 1990; Nadim et al. 2000; Labud et al. 2007). Depending on the remediation objective, it can be beneficial to either retard the movement of a contaminant or enhance its

removal (Ranjan et al. 2006), and it is therefore important to better understand better the mechanisms of these processes. The adsorption of neutral organic contaminants on clay minerals can be considerably impacted if the inorganic clay surface cations are replaced by a quaternary ammonium equivalent. Therefore, the influence of cationic surfactants, such as cetyl trimethylammonium bromide (CTAB), on the ability of a clay to retain nonionic inorganic solutes has been the subject of detailed study (Ranjan et al. 2006).

Multi-component organic/clay systems are in principle amenable to examination by small angle neutron scattering (SANS), and several such studies have been reported (Hanley et al. 1997, 2003; Hermes et al. 2006; King et al. 2007; Zhou et. al. 2007). Nevertheless, relatively few studies have addressed environmental problems, although there are some examples (Diallo et al. 2005). In the present study, we apply the SANS technique to investigate the adsorption of an aerospace fuel quadricyclane, C_7H_8 (Bai et. al. 2002; Lee et al. 2005) on an organic/clay system in the presence of an aqueous detergent.

SANS equations

The SANS technique (Higgins and Benoit, 1994) measures the scattered intensity, $I(q)$, as a function of the scattered wave vector, q, where $q = 4\pi \sin(\theta/2)/\lambda$, with λ the incident neutron wavelength. The straightforward expression for the scattered intensity from a simple system of units randomly dispersed in a given volume of a medium is

$$[1] \qquad I(q) \sim A\phi V_p(\rho - \rho_m)^2 P(q)$$

where A is an apparatus constant, ϕ is the volume fraction and V_p is the volume of a unit:

$P(q)$ is the form factor which is a function of the unit's geometry. The term $(\rho - \rho_m)^2$

represents the scattering power of the unit with respect to the medium. Here ρ is the scattering length density defined as $\rho = \rho_{mol} \sum b_j N(j)$ with ρ_{mol} the molar density, b_j the neutron scattering length of nucleus j, and $N(j)$ the number of nuclei of type j. The term ρ_m is the scattering length density of the background medium.

The model system

Quadricyclane is assumed to be sorbed on the clay complex through the organic matter in association with cationic species present in the contacting aqueous phase. We model this scenario by considering the synthetic clay sodium Laponite as the clay mineral, α-amino acid l-lysine as representative organic matter, and CTAB as a typical cationic detergent. Laponite platelets are of composition

$$Si_8\left[Mg_{5.54}Li_{0.46}H_4O_{24}\right]^{0.46-} Na^+_{0.46}$$
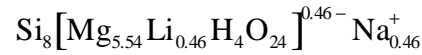
and the surface sodium ions can be totally or partially substituted by the cationic surfactant and/or by the lysine. In other words, the system can be considered as a particle made up of a central core and a surface coating. If the core has a characteristic scattering length density ρ_1, and the surface has a characteristic scattering length density ρ_2, the scattered intensity can be written

[2] $\qquad I(q) \sim \left\{ (\rho_2 - \rho_m)\left[V_T P_T(q) - V_1 P_1(q)\right] + (\rho_1 - \rho_m)V_1 P_1(q) \right\}^2$

where V_1 is the volume of the core, and V_T is the total volume of the particle.

In the limit that $q \to 0$ - which is of interest here - Eqn. [2] then becomes

[3]
$$I \sim \left\{ (\rho_1 - \rho_2)V_1 + (\rho_2 - \rho_m)V_T \right\}^2$$

Equation [3], however, can be written in a more practical form. A shift in the forward scattering for a sample in various solvents is proportional to the number of moles displaced by the scatterers, so that one can write the scattering power, Δ, of one mol of scatterer a that displaces x_{ab} mol of solvent b as

[4]
$$\Delta_{ab} = [\sum_{ia} b_i - x_{ab} \sum_{ib} b_i]^2$$

where b_i is now taken over all atoms in the unit. If one mol of the scatterer has now x_c moles of a surface component c attached to it, which displaces x_{cb} moles of solvent b. The scattering power becomes

[5]
$$\Delta_{acb} = [(\sum_{ia} b_i + x_c \sum_{ic} b_i) - \sum_{ib} b_i(x_{ab} + x_{cb})]^2$$

The ratio of the scattering powers for different values of the displaced mol fractions with be equivalent to the ratio of the measured scattered intensity as $q \to 0$.

Solutions, SANS configurations

A stock solution was prepared by stirring 0.5 g of laponite in 100mls of D_2O for five hours: the solution was clear and stable for many weeks. Solutions of lysine and CTAB were made up with concentrations equivalent to a five times multiple of the cation exchange

capacity (CEC) of the clay, which was taken as 76 mmoles equivalent/100g (Morvan et al. 1994) [Selecting this multiple of the CEC was arbitrary, but we have observed in our previous work (Hanley et al. 1997) that cationic/clay systems tend to aggregate heavily below this ratio.] All calculations are with respect to one mol of the laponite surface, molecular weight = 379.3g. Accordingly, 100ml D_2O/laponite mixtures with 0.275g lysine and 0.683g CTAB, respectively, were prepared by stirring, very lightly centrifuging and filtering. A laponite/lysine solution was also prepared in H_2O. Finally, 10ml mixtures were made up by adding various amounts of quadricyclane to a solution composed of CTAB added to previously mixed laponite and lysine.

Neutron scattering intensities from the solutions were obtained from the appropriate samples loaded in 1 mm gap-thickness quartz cells and placed in the beam of the 30 m SANS NG3 spectrometer of the US National Institute of Standard and Technology (NIST) Cold Neutron Research Facility. The spectrometer was configured: (a), with an incident neutron wavelength λ = 0.5 nm and a sample-detector distance of 4.5 m; and (b), with an incident neutron wavelength λ = 0.6 nm and a sample-detector distance of 13 m with the detector offset by 25 cm. The wave vector ranged for these configurations between 0.03 < q < 1.2 nm^{-1}. Scattered neutrons were detected on the instruments 2D position sensitive detector. Azimuthally averaged data were corrected for empty cell and solvent scattering as previously described (Hanley et al. 1997). All experiments were carried out at ambient temperature and atmospheric pressure.

Results and discussion

Figure 1 displays the SANS data from the solution with lysine adsorbed on the laponite. Two curves are shown: one indicating the scattering with H_2O as the solvent, the

other with D_2O. Inspection of Eqn. [5] indicates that the mole fraction, x_{ly}, of lysine adsorbed

on the clay can be determined from the two data sets. The experimental forward scattering

ratio $I(q)_{H_2O} / I(q)_{D_2O}$ as $q \to 0$ is approximately 2. From Eqn [5], given the parameters listed

in Table 1, we estimate this corresponds to $x_{ly} \approx 0.1$.   This mol fraction in turn corresponds

to a surface coverage of about 1/3 CEC equivalents. Hence, lysine is only partially adsorbed

on the clay surface.

Figure 2 illustrates the effects of adding CTAB. The scattering pattern from a

CTAB/laponite mixture in D_2O is shown as the middle curve in the figure. Given an

experimental ratio of the forward scattering of ~ 36, calculation using Eqn 5 suggests that

x_{CTB} is ~1.0 equivalent to approximately 3-4 CEC equivalents. This value is consistent with

our previous independent estimate reported by Hanley et. al. (1997). When, however, CTAB

is added to a solution of the laponite pre-mixed with lysine, the scattering is enhanced as

indicated by the upper curve in the figure. From the experimental forward scattering ratio,

and using Eqn. 5, with $x_{ly} = 0.1$, we estimate that the CTAB coverage has increased to x_{CTB} ~

1.8 which corresponds to about 6 CEC equivalents. Thus the presence of a relatively small

amount of adsorbed lysine considerably increases the adsorption of the CTAB on the

laponite.

The effect of adding quadricyclane and CTAB to previously mixed laponite and lysine

in D_2O is shown in Fig. 3. The upper curves depict the scatter with (a) 0.035ml and, (b) 0.7

ml quadricyclane added to the 10ml solution. From the forward scattering ratio and setting

$x_{ly} = 0.1$ and $x_{CTB} = 1.8$ in Eqn.5, we estimate that $x_{quad} = 3.5$ mixture (a) and $x_{quad} = 6.5$ for

mix (b). Using the quadricyclane density of 0.982g cm^{-3} these estimates are equivalent to ~

0.04mls and ~ 0.08mls adsorbed in 10mls, respectively. When compared to the original

concentrations, given the experimental uncertainty in all the forward scattering extrapolations,

we conclude that essentially all of the quadricyclane was probably adsorbed from mixture (a) but that there is a surplus in mixture (b). We could thus assume that there is a threshold concentration above which further quadricyclane adsorption would not occur.

The results reported here reinforce quantitatively the work of previous authors who have pointed out the importance of a cationic surfactant in the mechanism of pollutant/clay adsorption, either in the context of remediation or in the context of retention. We have, however, demonstrated the major contribution of the organic matter, lysine, to the overall adsorption mechanism.

We conclude by remarking that it would be relatively straightforward to extend this brief study - to obtain the quadricyclane adsorption isotherm, for example. The SANS technique could also be applied to elucidate the nanostructure of the clay surface and of the components in the liquid phase. Overall, we have demonstrated that the SANS technique can be a valuable adjunct to a general study of environmental contamination.

Acknowledgement

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Table 1. Neutron scattering parameters - molecular mass, the sum of the atomic scattering lengths and the scattering length density (sld).

	Mass g	Scattering length 10^{12} cm	sld 10^{-10} cm^{-2}
Laponite	379.3	9.452	3.80
CTAB	363.9	-1.453	-0.24
CTA$^+$	284	-2.133	-0.45
Lysine	147	1.42	0.58
Lysine, Cl$^+$	182.5	2.38	0.78
Quadricyclane	92	1.663	1.07
H_2O	18	-0.168	-0.56
D_2O	20	1.914	6.37

Figure 1.   Plot of the scattered intensity from a solution of lysine adsorbed on laponite: in D_2O (lower curve) and in H_2O (upper curve).

Figure 2.   Plot of the scattered intensity from D_2O solutions of CTAB (CTA^+) adsorbed on laponite. Lower curve - scattering from laponite; middle curve - scattering from CTA^+ on laponite; upper curve - scattering from CTA^+ adsorbed on laponite precoated with lysine.

Figure 3. The two upper curves show the scattered intensity from two D_2O solutions of quadricyclane/CTAB mixtures adsorbed on laponite precoated with lysine. The solutions contained 0.7ml (squares) and 0.035 ml of quadricyclane in 10ml of the laponite complex mixture (circles). The lower curve (diamonds) is the scattering from laponite in the absence of quadricyclane and CTAB. The enhanced scattering due to adding the quadricyclane is seen by comparing the upper curves of this figure with the upper curve of Fig. 2.
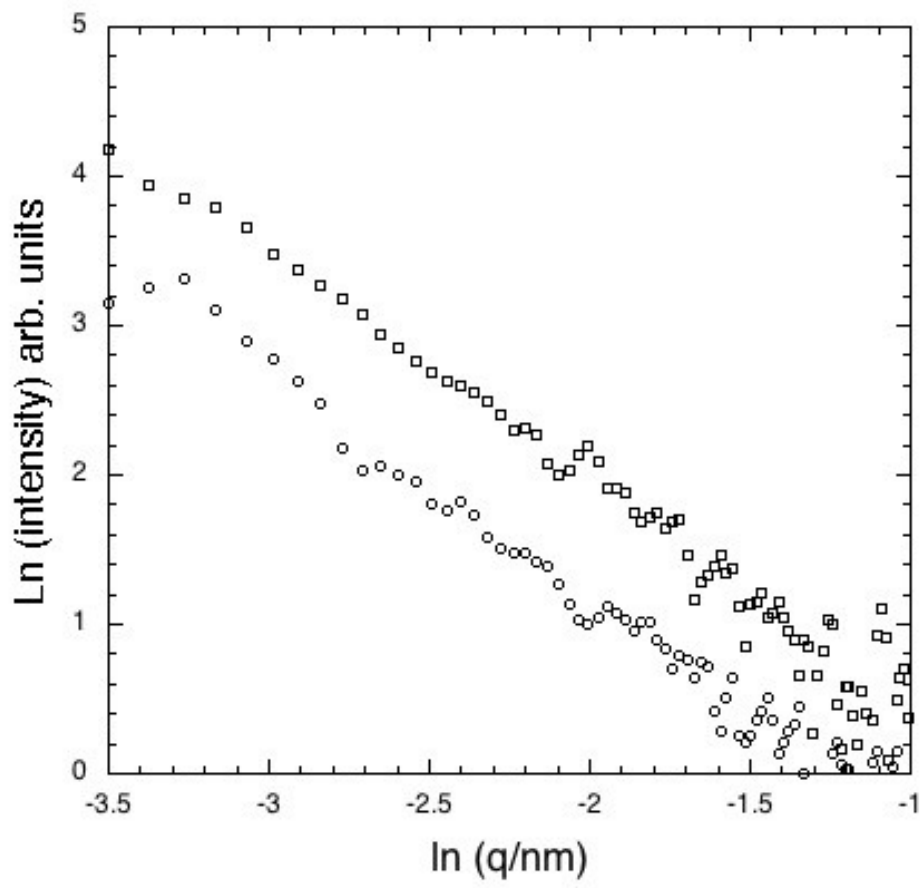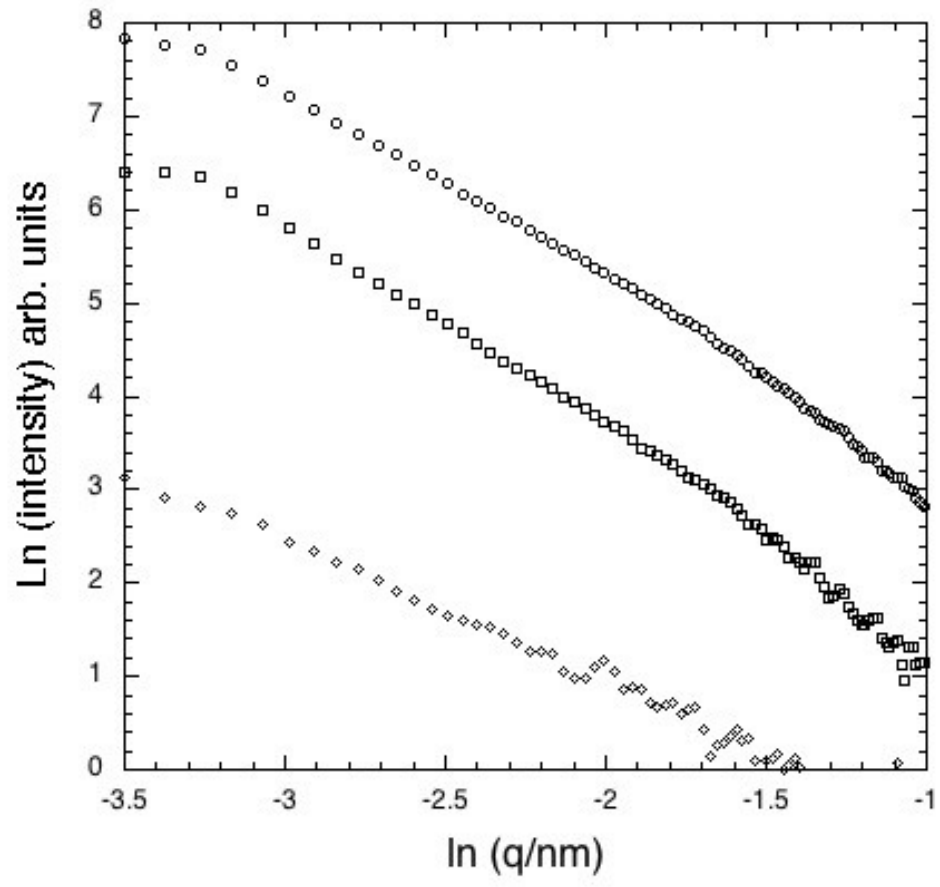
Fig 1.

Fig. 2.

Fig. 3.