REACTIONS OF AMMONIA WITH SOIL, III SORPTION OF AQUEOUS NH₃ BY HOMOIONIC SOIL CLAYS

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Summary

Homoionic clay suspensions were equilibrated at $25°C$ with aqueous NH_3 (0.01 to 0.30 M) by agitating for several days. Using clays extracted from three different soils, sorption of NH_3, measured by titration, followed the order $Na > Ca > NH_4$-clay. The difference in NH_3 sorption between Na-clay and NH_4-clay was matched by an increase in Na^+ ion concentration in the aqueous phase of suspensions of Na-clay treated with NH_3, but there was no such effect with Ca-clay.

Sorption of NH_3 on NH_4-clay in aqueous suspension is considered due to proton donation at sites of pH-dependent charge, and the additional sorption on Na-clay to displacement of Na^+ by NH_4^+ ions. The additional sorption on Ca-clay seems largely due to co-ordination of Ca^{2+} ions with molecular NH_3. Exchangeable cations affect NH_3 sorption differently when an aqueous phase is present than when dried homoionic materials are treated with NH_3 gas.

Introduction

LARGE-SCALE use of ammonia as a fertiliser began in the 1930s when it was added to irrigation water in Californian orchards. Jenny *et al.* (1945) studied sorption of aqueous NH_3 on Californian soils, and the availability of sorbed NH_3 to plants and nitrifying bacteria.

Since the 1950s, most NH_3 has been injected into soil in bands, either as aqueous or, especially in the U.S.A., as anhydrous NH_3. Almost all subsequent research (see McVickar *et al.*, 1966, for reviews) has involved using NH_3 gas and dried soil or clay. However, studies involving an aqueous phase have an obvious relevance to practical agriculture, and the various mechanisms proposed for NH_3 sorption on dried materials might have different relative importance under aqueous conditions.

Various workers, using dried homoionic soils and clays, have studied the effects on NH_3 sorption of altering the exchangeable cation. Some (Mortland *et al.*, 1963; James and Harward, 1964; Russell, 1965; Mortland, 1968) have emphasised the importance of sorption mechanisms actually involving exchangeable cations; previous papers in this series (Ashworth, 1973 and 1978) have drawn attention to the contribution to overall sorption due to reaction of NH_3 at sites of pH-dependent charge.

To establish the importance of exchangeable cations in determining sorption of NH_3 from aqueous solution, NH_4-clay was used as a standard of comparison with other forms of clay. Although, in presence of an aqueous phase, NH_3 can be sorbed through displacement of resident cations into solution by NH_4^+ ions, no net sorption via this mechanism can occur on homoionic NH_4-clay. Also, although

exchangeable cations also co-ordinate directly with NH_3, this is unlikely in the case of NH_4^+ ions.

Ammoniates of ionic salts are most stable when the cation is small or highly charged (Jolly, 1964). However, Bjerrum (1941) showed that, in dilute aqueous NH_3 (<0.5 M), even Mg^{2+} ions have little tendency to be co-ordinated by NH_3: Ca^{2+} and Li^+ ions even less, and Ba^{2+} and K^+ ions none at all. This, and the similarity in size of K^+ and NH_4^+ ions, indicate that little NH_3 will be co-ordinated with exchangeable Ca^{2+} ions, and less, if any, with Na^+ or NH_4^+ ions on clay suspensions in dilute aqueous NH_3.

It was known from previous work that exchangeable Na^+ ions can contribute to aqueous NH_3 sorption, because sorption was substantially more on Na- than on Ca-bentonite at a given equilibrium NH_3 concentration (Ashworth, 1972). In the work described here, Na- and Ca-clays were used in order to repeat this comparison using soil clays.

Experimental

Various difficulties were met in preliminary attempts to estimate sorption from the fall in concentration of NH_3 in solutions added to clays. To obtain reproducible sorption isotherms it was found necessary to agitate the mixture for 2 to 3 days and especially to use small ratios of clay:solution. The change in NH_3 concentration was therefore small and its measurement was not reproducible with very satisfactory precision, even allowing for errors in titration. Errors caused by evaporation of NH_3 after centrifuging the equilibrated mixture were largely avoided by acidifying portions of the supernatant solution and back-titrating with standard alkali, instead of titrating directly with standard acid.

Suspensions in aqueous NH_3 (0.02 M) of soils with more than 2 per cent C gave yellow, cloudy supernatant solutions on centrifuging and considerable pH buffering was observed during back-titration. Soils with less than 1 per cent C gave clear, colourless, unbuffered supernatant solutions. Pre-treatment of soil with H_2O_2 to remove organic carbon was avoided after it was found in preparative work (Ashworth, 1971) that this made it very difficult to obtain completely saturated, homoionic Na-soil.

Materials and methods

Batcombe soil was obtained from the plot receiving no fertiliser in the long-term wheat experiment on Broadbalk field, Rothamsted; Bromyard and Speller soils from sub-surface horizons (all soils had less than 1 per cent C). The clay fractions were separated by standard sedimentation methods and Na-saturated suspensions prepared as described by Deist (1966). Portions were re-saturated with NH_4^+ or Ca^{2+} ions by repeated treatment with NH_4OAc or $CaCl_2$ solution. All the suspensions were washed salt-free with water and the clays recovered by washing with ethanol, then petroleum ether. The air-dried materials were stored at room temperature ($22 \pm 2\,^\circ C$) in equilibrium with saturated $Mg(NO_3)_2$ solution (relative humidity = 0.55).

Cation exchange capacities (CEC) were measured by leaching with NH_4OAc solution (1 M) and analysing the leachate spectrophotometrically for Na^+ or Ca^{2+}. NH_4^+ was measured by titrating NH_3 evolved on alkaline steam distillation of a portion of clay. Surface areas were measured by the ethylene glycol method of

TABLE 1
Properties of parent soils and their clay fractions

Soil series	clay %	mineralogy	carbon* %	Clay fraction	
				CEC (meq kg^{-1})	Surface area ($m^2\,g^{-1}$)
Batcombe	24	mainly expanding minerals	0.80	NH_4 320 Na 330 Ca 420	282 285 369
Bromyard	45	contains moderate chlorite	0.40	NH_4 260 Na 270 Ca 300	202 220 283
Speller	58	contains mainly illite	0.83	NH_4 210 Na 230 Ca 250	243 220 303

*Tinsley method.

Rawson (1969). These data and some properties of the parent soils are collected in Table 1.

Thorough equilibration of clays with aqueous NH_3 was achieved as follows: clay samples (0.5 g) and water (20 cm^3) were magnetically stirred (500 r.p.m.) for 24 h at 25 $^\circ$C in flasks closed with greased ground glass stoppers, to ensure thorough dispersion of the clay particles. Aqueous NH_3 (0.05–1.5 M, 5 cm^3) was added and stirring continued for a further 3 days at 25 $^\circ$C.

The suspensions were then pipetted into two centrifuge tubes (15 cm^3 capacity) and centrifuged at 25 $^\circ$C (18 000 r.p.m., 30 min). To measure sorption, two portions of the supernatant solution (5 cm^3) were pipetted into a known excess of HCl (5 cm^3), then back-titrated directly with standard NaOH, monitoring pH by glass electrode. Another two acidified portions were back-titrated after alkaline steam-distillation into the same known excess of HCl. In all titrations, the burette was read at the pH (*ca.* 5.3) corresponding to that calculated for a solution of NH_4Cl of appropriate concentration. Buffering action due to dissolving CO_2 was apparent near pH 6 but did not affect the measurements. 'Control' suspensions of clays treated with water, and samples of aqueous NH_3, underwent the whole procedure and were titrated similarly.

In similar experiments, the change in Na^+ or Ca^{2+} ion concentration in the supernatant solution, relative to the value in suspensions of the appropriate clay in water, was measured spectrophotometrically.

Sorption of aqueous NH_3 by silica gel (Fisons, for chromatography) was measured for the purpose of comparison with the results obtained with clays. Equilibration was rapid and the amount of NH_3 sorbed was unaffected by the SiO_2-gel:solution ratio.

Integral heats of reaction between aqueous NH_3 and Na^+ and Ca^{2+}-saturated Batcombe clay were measured in a batch microcalorimeter (LKB type 10700), as described by Hayes *et al.* (1972). Clay suspensions (4 cm^3, 20 g clay/l) and aqueous NH_3 (2 cm^3, 0.002–0.02 M) in divided compartments of one cell of the instrument, and matching quantities of suspension and water in the twin cell were first brought to 25 $^\circ$C. The amount of NH_3 sorbed after 30 min. in matching experi-

ments in stoppered tubes was measured after centrifuging, by tit▢▢ ▢▢ ▢e super-
natant solution as already described. In these experiments, clay and NH_3 did not
reach equilibrium.

Results and discussion

The NH_3 sorption isotherms (Figs. 1a, b and c) were calculated from the
amounts of NH_3 in supernatant solutions and in 'control' solutions of NH_3, as
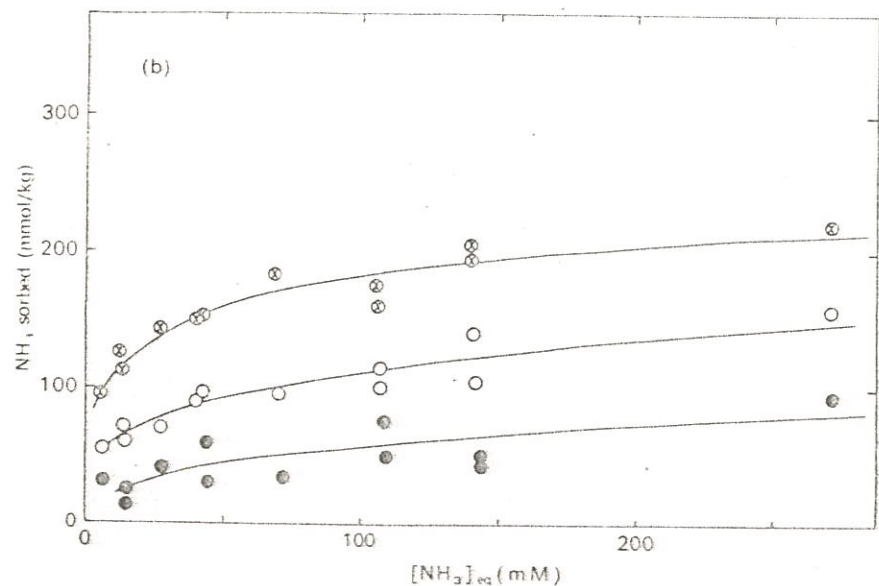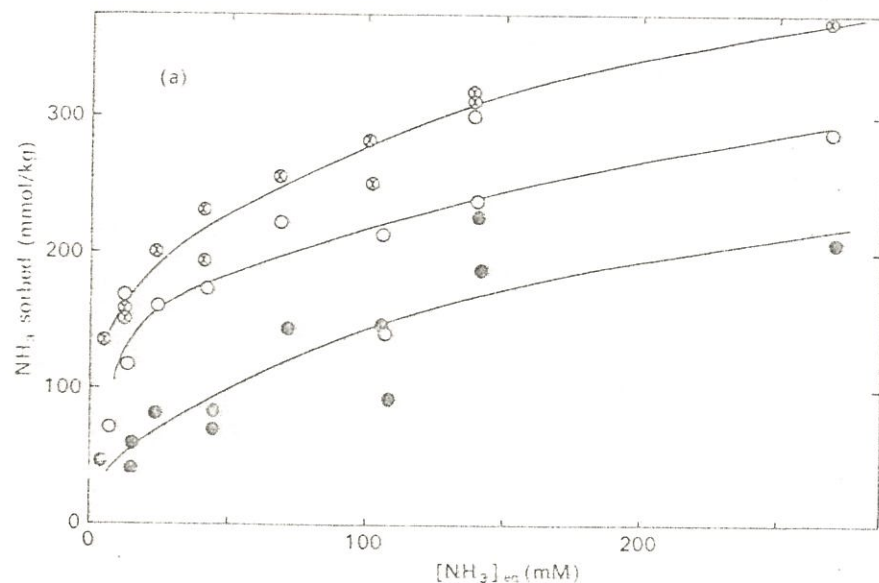
indicated by the ▢▢x-▢▢▢ations obtained after steam distillation (typical results are
in Table 2).

Amounts of NH_3 sorbed (A), at any equilibrium NH_3 concentration $[NH_3]_{eq}$,
follow the order $Na > Ca > NH_4$-clay with all three clays. Replication of data is
generally poor, but perhaps less so for Na-clays, suggesting that clay dispersion was
still incomplete. Despite the error involved (we estimate ±15 per cent of A), the
differences between the curves for Na-, Ca- and NH_4-clays are consistently greater
than this, suggesting that NH_3 reacts with Na^+ and Ca^{++} ions.

The observed increase in sodium ion concentration (δNa^+) in the aqueous phase
of Na-clay suspensions treated with NH_3 is approximately equivalent to half the
CEC (Fig. 2). With Na-soil, there was a difference (B) between back-titres obtained
after steam distilling the supernatant solution, and after adding it directly to excess
HCl. Values of B were small and carry the accumulated errors of two titrations
(results in Table 2 have not been rounded, because then B would also carry
rounding errors). Values of δNa^+ are also subject to two sets of errors in determina-
tion. With due allowance for these errors, a trend towards equivalence between
these parameters can be seen (Fig. 3) which is consistent with the sorption
mechanism:

$$Na\text{-clay} + NH_3 + H_2O \rightleftharpoons NH_4\text{-clay} + Na^+ + OH^- \qquad (1)$$
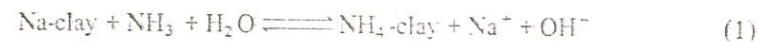
since hydroxyl ions are not volatile and therefore affect only the direct back-
titration.

With all three clays, values of δNa^+ correspond to the difference in NH_3
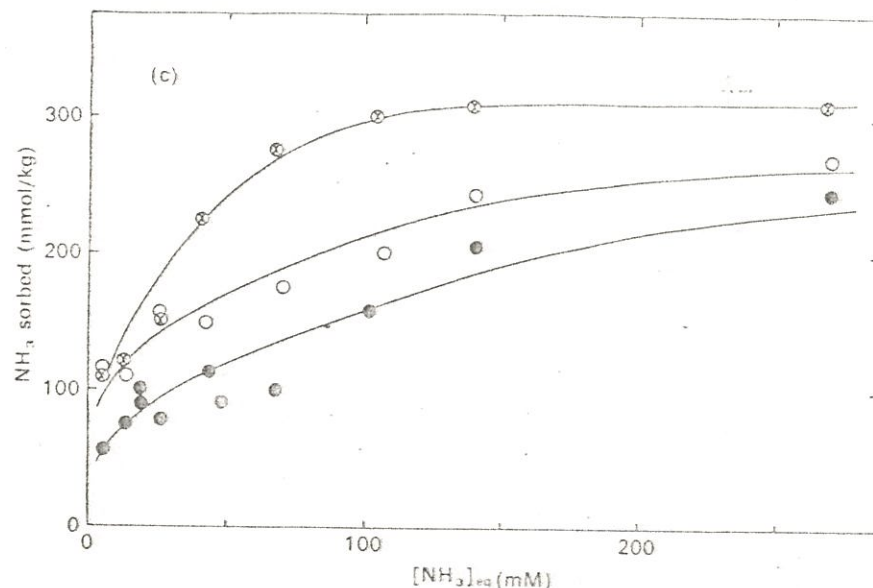sorption between Na-clay and NH_4-clay (ca. 125 meq/kg clay over most of the

FIG. 1. Amounts of NH_3 sorbed (A) on clays at equilibrium with aqueous NH_3 of con-
centration $[NH_3]_{eq}$: (a) Batcombe, (b) Bromyard, (c) Speller clay; ⊗ Na-form, ○ Ca-form, ●
NH_4-form.

TABLE 2
Results of treating Speller clay with 0.01 M NH_3

Homoionic cation	Mean back-titres			A $= 50 (v_2 - v_1)$	B $= 50 (v_2 - v_3)$	δNa^+
	v_1*	v_2**	v_3***			
	(cm^3 0.005 M NaOH)			(meq/kg clay)		
Na		11.22	9.26	144	98	110
Ca	8.35	10.86	10.84	125	1	–
NH_4		9.52	–	59	–	–

*5 cm^3 control NH_3 solution steam distilled into HCl.
***5 cm^3 supernatant solution steam distilled into HCl.
***5 cm^3 supernatant solution added directly to HCl.
– not measured, or inapplicable.

range of NH_3 concentrations employed). The ion-exchange reaction shown in Equation (1) accounts satisfactorily for the extra NH_3 sorption on Na-clays; this supports the view (see Introduction) that direct co-ordination to Na^+ is insignificant in dilute NH_3.

With Ca- and NH_4-clays, the quantity B was always near zero, and NH_3 treatment caused little change in Ca^{2+} ion concentration in the aqueous phase of Ca-clays. A substantial part of the extra NH_3 sorption on Ca-clays, relative to that on NH_4-clay (ca. 65 mmol per kg clay over most of the range) is probably due to co-ordination of Ca^{2+} ions with NH_3. In $CaCl_2$ solution 10 per cent of the Ca^{2+} ions are co-ordinated with a molecule of NH_3, in 0.2 M aqueous NH_3 (Bjerrum, 1941).
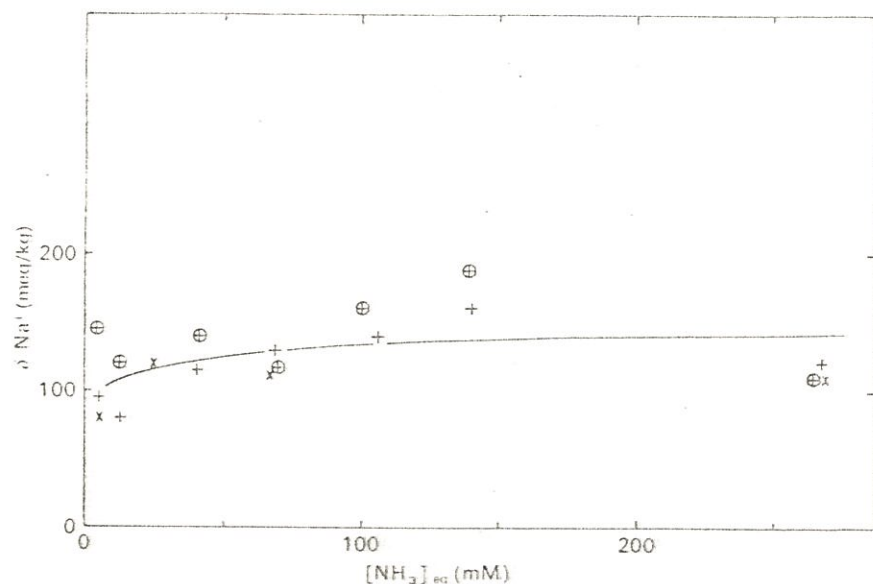
FIG. 2. Change in sodium ion concentration (δNa^+) in aqueous phase of clay suspensions equilibrated with aqueous NH_3 $\oplus$ Batcombe, + Bromyard, x Speller clay.
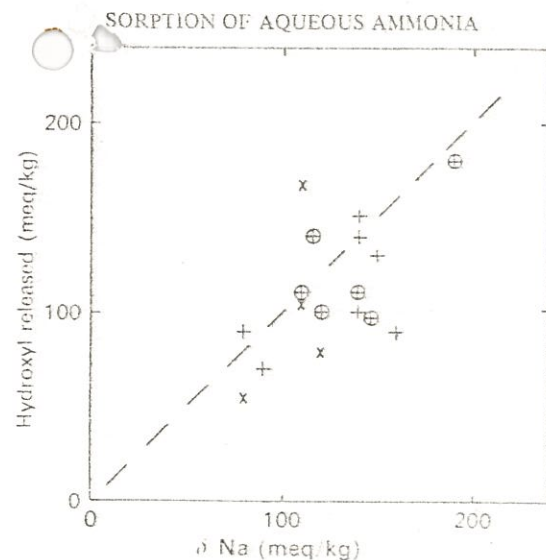
FIG. 3. Correlation between δNa^+ and the amount of hydroxyl ion released (B) after equilibration: legend as for Fig. 2.

If exchangeable Ca^{2+} ions on clay suspensions at equilibrium with 0.2 M NH_3 behaved similarly, co-ordination would account for only 20 mmol NH_3 per kg clay; however, co-ordination complexes involving ions held at fixed sites may be more stable than those with ions free in solution.

$Ca(OH)_2$ is too soluble for Ca^{2+} ions in the aqueous phase to be precipitated as the hydroxide, even at high pH. Therefore, the reaction:

$$Ca\text{-clay} + 2NH_3 + 2H_2O \rightleftharpoons (NH_4)_2\text{-clay} + Ca(OH)_2 \qquad (2)$$
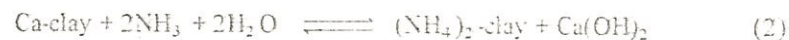
could contribute to NH_3 sorption only on the assumption that any $Ca(OH)_2$ formed remained trapped at the site of reaction, since no increase in Ca^{2+} ion concentration in the aqueous phase was detected. However, Mortland and Raman (1968) found that sorption of NH_3 vapour by means of reaction (2) was extremely sensitive to the degree of hydration of Ca-clay films, falling from 800 to 160 mmol/kg bentonite as relative humidity rose from 0.20 to 0.98. The contribution to sorption from this mechanism is therefore likely to be very small under aqueous conditions, but cannot be ruled out. Calcium carbonate is much less soluble than the hydroxide, but the reaction:

$$Ca\text{-clay} + 2NH_3 + H_2O + CO_2 \rightleftharpoons (NH_4)_2\text{-clay} + CaCO_3 \downarrow \qquad (3)$$

cannot have contributed significantly to NH_3 sorption. The quantity of CO_2 in the system was equivalent to less than 5 per cent of the CEC, and deliberately adding CO_2 (as CO_2-saturated water) in amounts equivalent to 100 per cent of the CEC increased sorption by only about one third, in tests using Ca-saturated Bromyard and Speller clays.

A substantial proportion of sorption on Na- and Ca-clays, and practically all sorption on NH_4-clays, apparently involves mechanisms independent of the exchangeable cation. The most likely mechanism is protonation of NH_3 at sites of
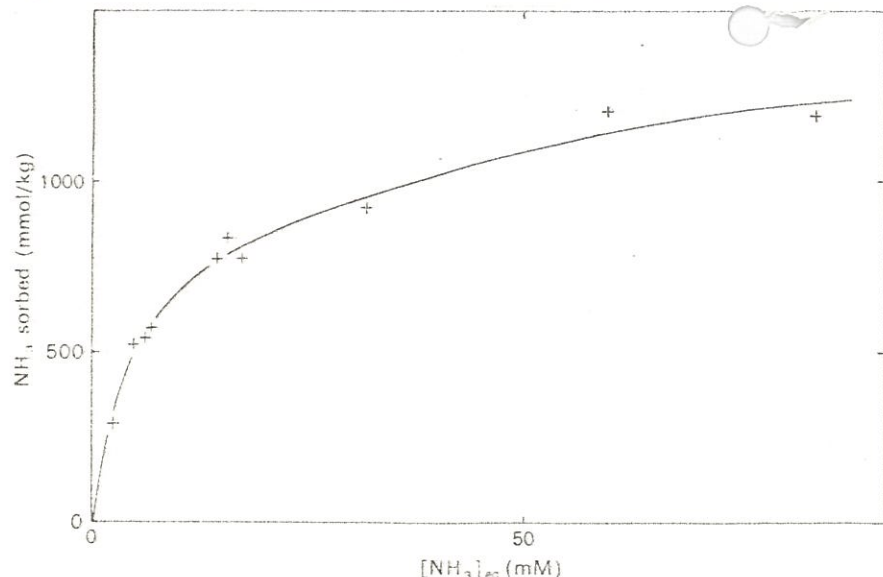
FIG. 4. Sorption of aqueous NH_3 on SiO_2 gel.

FIG. 5. Integral heats of sorption of NH_3 on Batcombe soil: ⊗ Na-form, ○ Ca-form.

pH-dependent charge, such as the silanol hydroxyls at broken edges of aluminosilicate lattices mentioned by Jenny *et al.* (1945) and by many workers since. The ability of silanol groups to sorb NH_3 is demonstrated by the sorption isotherm obtained with silica gel (Fig. 4), for which sorption, and surface area to ethylene glycol (1290 m^2 g^{-1}), are roughly 5 times greater than for the clays studied.

Because the clays contained a residue of organic matter, NH_3 may also have reacted with phenolic and carboxylic hydroxyls. Young (1964) found that the amount of NH_3 'strongly sorbed' by soils was correlated both with clay content and organic carbon. However, organic matter in the materials we used would probably contain few labile groups and make only a minor contribution to sorption.

Various workers (McVickar *et al.*, 1966) have suggested that hydrogen bonding could contribute to NH_3 sorption on clays. Under our conditions, since NH_3 is already H-bonded to water molecules, these bonds must break when others are formed to the clay surface, which implies a negligible enthalpy change for the overall process. Sorption mechanisms with very small ΔH cannot contribute by more than about 1 per cent to overall sorption, as long as sites remain unoccupied where ΔH of sorption is at least 10 kJ/mol (assuming all sorption mechanisms have similar entropy). The heats of NH_3 sorption on Na- and Ca-clays (Fig. 5) are well in excess of this figure. Also, even in the absence of an aqueous phase, no evidence for H-bonding of NH_3 to the clay surface has been found (Russell, 1965; Ashworth, 1978). These observations suggest that a mechanism involving H-bonding is unlikely to contribute significantly to sorption from aqueous NH_3.

It is noteworthy that the different ΔH values obtained with Na- and Ca-saturated Batcombe clay are consistent with two different mechanisms of sorption from dilute aqueous NH_3.
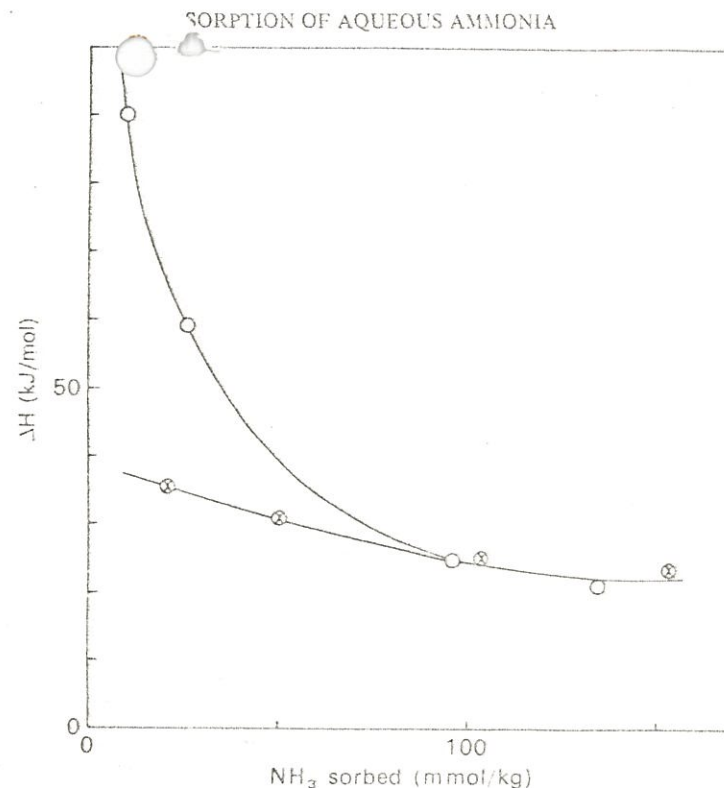
Previously (Ashworth, 1973), differences between amounts of exchangeable mono- and divalent ions (such as those in Table 1) were ascribed to a preference for divalent ions on the part of exchange sites on organic matter (Addiscott, 1970). However, this explanation cannot wholly account for the extra Ca^{2+} ion extracted by NH_4OAc from Batcombe soil clay. This indicates the presence of a Ca salt which could, through NH_3 co-ordination, make our estimate of A on Ca-saturated Batcombe clay erroneously high. The estimate of ΔH should, however, be little affected, since ΔH of co-ordination of Ca^{2+} ions should be insensitive to the nature of the counter-ion.

Suspensions of all forms of all soil clays equilibrated with aqueous NH_3 were analysed for Al and Si after centrifuging. All gave similar results: very small amounts (<1 mg/l) of Al and Si were found, except that Si concentrations rose sharply with increasing $[NH_3]_{eq}$ above 0.1 M, reaching 6 mg/l at $[NH_3]_{eq}$ = 0.25 M. However, the set of determinations of A made for each clay at this value of $[NH_3]_{eq}$, though unreplicated, gave results in line with those obtained at lower concentrations, suggesting that clay mineral dispersion had little effect on our measurements.

General conclusions

In previous work (Ashworth, 1973) on dried, homoionic Batcombe soil, amounts of NH_3 gas sorbed followed the order Ca > NH_4 > Na-soil. The sodium

form sorbed least NH_3, apparently because little or no NH_3 is co-ordinated with Na^+ ions, whereas NH_3 can be H-bonded to NH_4^+ ions under the relatively anhydrous conditions employed, and can either be co-ordinated with Ca^{2+} ions or, through reaction (2) with water of cation hydration, form NH_4^+ ions plus $Ca(OH)_2$.

The results described here, and the suggested interpretation, are much more relevant to practical agriculture than previous work in systems with no aqueous phase. However, results from both sets of conditions agree in showing that soils have a large adsorption capacity for NH_3 which is independent of the exchangeable cation. The importance of sorption mechanisms that involve exchangeable ions has perhaps become over emphasised as a result of related work on pure homoionic clays (Mortland *et al.*, 1963; James and Harward, 1964; Russell, 1965; Mortland, 1968). The density of pH-dependent charge sites on a particular soil is more important for NH_3 sorption than its degree of Ca saturation.

However, interaction of Ca^{2+} ions with NH_3 can be expected to be significant in sorption at the centre of injected bands, where NH_3 is concentrated. Also, at the periphery, some exchange of NH_4^+ for Ca^{2+} ions can be expected, by means of Equation (3), because of CO_2 absorption from the soil atmosphere outside the band. This reaction cannot contribute significantly to NH_3 sorption taking place immediately on injection, as suggested by du Plessis and Kroontje (1966), because very little CO_2 is present in the volume of soil encountered by the injected NH_3. However, CO_2 absorption will assist afterwards in gradually bringing the alkaline soil solution in the injected band to a pH suitable for ammonium oxidising bacteria.

Acknowledgements

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