

NOTE

THE ION EXCHANGE ADSORPTION OF ALKYLAMMONIUM IONS:  
AN ALTERNATIVE VIEW

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It is a well-known observation that the adsorption strength of alkylammonium ions in montmorillonite increases regularly with molecular weight (Cowan and White, 1958; Theng *et al.*, 1967; Vansant and Uytterhoeven, 1972; Theng, 1974). Usually, the affinity enhancement with molecular size is interpreted in terms of an increasing contribution of van der Waals forces to the adsorption strength. Although such a view is acceptable for the homologous series of monoalkylammonium ions, it is not wholly satisfactory for di- and trialkylammonium ions since these ions are generally more strongly adsorbed than can be expected on the basis of molecular weight, i.e. compared to the straight chain alkylammonium ions of similar molecular weight. For example, the adsorption affinity of trimethylammonium ion, as referred to sodium, exceeds the value for propylammonium by some 2.5 kJ/mole (Theng *et al.*, 1967), in spite of identical molecular weights; in contrast, the difference between methyl- and butylammonium is only 1.3 kJ/mole.

To account for this apparent discrepancy, Theng *et al.* (1967) hypothesized that the increased contribution of van der Waals forces to the adsorption strength, due to an increased substitution of hydrogen by alkyl groups, more than compensates for the reduction in affinity, due to a decrease in the number or strength of hydrogen bonds between the amine cation and the oxygen atoms of the silicate surface. Plausible as this *ad hoc* hypothesis may sound from the qualitative point of view, it does seem unrealistic in quantitative terms in regard to the assignment of such large differences in adsorption strength for ions of identical molecular weight, exclusively in terms of van der Waals forces.

We propose a radically different view through an extension of the quantitative concept of thermodynamic stability of alkylammonium ions in the clay interlayer space. We have recently shown (Maes *et al.*, in press) that the increase in adsorption affinity of metal uncharged ligand complexes, as compared to the aqueous metal ion, may be identified with the gain in thermodynamic stability, acquired by the metal complex upon adsorption, relative to its value in solution. In a purely formal way, there is a similarity between the formation of a metal-amine complex and the formation of an alkylammonium ion from a proton and the amine. Therefore, we may define the stability of the adsorbed alkylammonium ion  $LH^+$  in an entirely similar fashion. These formation or stability constants are defined as

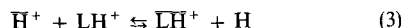
$$k = \frac{(LH^+)}{(L)(H^+)} \tag{1}$$

$$\bar{k} = \frac{(\bar{L}H^+)}{(\bar{L})(\bar{H}^+)} \tag{2}$$

$k$  and  $\bar{k}$  refer to the bulk solution and the ion exchanger. The activity terms in the bulk solution are defined on the molal scale, the activity terms for the ionic species in

the exchanger ( $\bar{L}H^+$ ) and ( $\bar{H}^+$ ) are defined on the equivalent fraction scale and for the amine  $\bar{L}$  on the molal scale. Within the terms of these definitions, no assumptions are made whatsoever regarding the controversial question as to hydrogen ion activity differences in the two phases.

Consider the ion exchange equilibrium:



for the reversible displacement of the hydrogen ion by the alkylammonium ion: the corresponding equilibrium constant is defined as

$$K = \frac{(\bar{L}H)(H)}{(\bar{H})(LH)} \tag{4}$$

in which, as before, the ion exchanger composition is specified on the equivalent fraction scale while the molal convention is used for the bulk solution. Expliciting  $(\bar{L}H)$  and  $(LH)$  in terms of equations (1) and (2) we obtain

$$K = \frac{k'}{k} p \tag{5}$$

in which  $p$  is the partition coefficient of the amine. This shows that, apart from the partition coefficient, the thermodynamic constant  $K$  for the  $H^+ - LH^+$  equilibrium is identical with the excess stability  $k'/k$  of the alkylammonium ion in the clay.

Due to some irreversible phenomena, related to structure breakdown of montmorillonite (Eeckman and Laudelout, 1961), the experimental evaluation of the thermodynamic constant, involving hydrogen ion equilibria is somewhat dubious. Nevertheless, data are available showing that the hydrogen ion selectivity, as expressed with respect to sodium, is close to unity; in the case of bentonite, Foscolos and Barshad (1969) report a value of 1.6 for  $K_{Na-H}$ , whereas a value of about 0.6 is reported for montmorillonite by Gilbert and Laudelout (1965). In any case, this is of limited relevance within the present context and we may equally well determine the adsorption affinity with respect to sodium, as is often the case.

The stability sequence of alkylammonium ions in aqueous solution exhibits the well-known 'amine anomaly', i.e. the expected inductive effects of the organic carbon chain are screened off by the solvent. In contrast, the literature data on the adsorption affinity of alkylammonium ions in montmorillonite, which are a direct measure of excess stability in the ion exchanger, exhibit a more natural sequence. This is illustrated clearly in Figure 1, which shows the correlation between the free energy terms for the displacement of sodium by alkylammonium ions (Theng *et al.*, 1967; Vansant and Uytterhoeven, 1972) vs the amine gas phase basicities (G.B.), relating to the gas phase reaction (Aue *et al.*, 1972).



The much closer correlation of alkylammonium ion

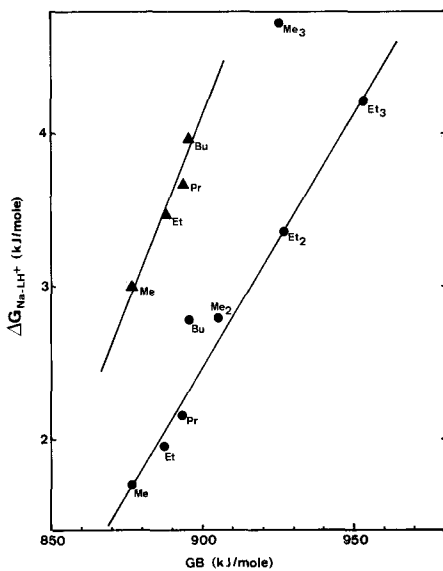


Figure 1. Correlation between free energies of exchange of sodium for alkylammonium ions and the amine gas phase basicities. Ion exchange data are taken from Vansant and Uytterhoeven (▲) and Theng *et al.* (●).

adsorption affinity with G.B. values, as compared to the molecular weight correlation, necessitates various comments. First of all, it puts the unexpectedly high affinities of di- and trialkylammonium ions in a proper perspective in demonstrating that the order of stability enhancement coincides exactly with the gas phase basicity sequence (of course, some reservations should be made with regard to the somewhat suspiciously high value for the trimethylammonium ion). This would indicate that the solvent screening effect is less operative in the clay interlayer space, as shown by the display of a true amine basicity order. Of course, this tendency remains very limited as shown by the fact that the 'stability difference' between methyl- and butylammonium is about 1 kJ/mole in the clay and 18 kJ/mole in the gas phase (it is essentially zero in bulk solution). In any case, the foregoing analysis tends to demonstrate that the extent of ion hydration is lowered upon adsorption in the clay interlayer space, i.e. a conclusion which may be of relevance to ion exchange phenomena in general.

A second comment relates to charge density effects. It is apparent from the data in Figure 1 that stabilization effects are more pronounced in the Camp Berceau montmorillonite (Vansant and Uytterhoeven, 1972), which displays a slightly higher charge density than the clay used by Theng *et al.* (1967). This effect has been confirmed in some recent studies in this laboratory and will be treated in a subsequent paper.

In conclusion, we wish to emphasize that this analysis is not intended to demonstrate that van der Waals forces are not operative in the ion exchange adsorption of alkylammonium ions: quite the contrary! It merely demonstrates that the clay interlayer space provides a medium which is conducive to the formation of more stable alkylammonium ions, this tendency resulting from various kinds of intervening factors, such as hydration changes and van der Waals forces.

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Centrum voor Oppervlaktescheikunde  
en Colloidale Scheikunde,  
Katholieke Universiteit Leuven,  
de Croylaan 42  
B-3030 Heverlee, Belgium

A. MAES  
P. MARYNEN  
A. CREMERS

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