MODELLING TITRATION CURVES OF MIXED MATERIALS WITH VARIABLE
AND PERMANENT SURFACE CHARGE: APPLICATION TO MIXTURES OF AN
IRON OXIDE AND MONTMORILLONITE.

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Two well-known materials, lepidocrocite (specific sur -
face area 116 m^2g^{-1}) and montmorillonite (internal surface
area 700 m^2g^{-1}), can be useful to test the mathematical mo-
del described in the preceding communication. With this pur-
pose, acid and base titration curves of both minerals and
of mixtures containing 80% (w/w) of lepidocrocite (sample
LM) and 80% montmorillonite (sample ML) were obtained at
three ionic strengths (0.01, 0.1 and 1 M NaCl). The amounts
of titrant consumed by the suspensions at each pH were cor-
rected for the amount consumed by the corresponding solu -
tion at the same pH. The resulting graphs are shown in next
page. Dashed lines will be explained later.

It is readily evident that the curves corresponding to
pure lepidocrocite and LM are very similar to those ob -
served in the literature for oxides and many variable
charge soils, with a crossover point (point of zero salt
effect, PZSE) approximately corresponding to the zero point
of titration. Sposito (1984) concluded that the point of
zero net charge (PZNC) and the PZSE are equal for solids
with no specific affinity for the electrolyte ions, so that
in the PZSE $\sigma_{ox} + \sigma_{cl}$ (σ_H of Sposito, 1984) equals $-\sigma_p R$ as
long as $\sigma_\beta \simeq 0$. A study of a wide variety of outputs of the
model (Madrid and Diaz-Barrientos, in press) showed that
when a crossover point was apparent in $\sigma_{ox} + \sigma_{cl}$ vs. pH plots
it happened at $\sigma_{ox} + \sigma_{cl} = -\sigma_p R$, in agreement with the conclu-
sion of Sposito (1984). This result provides a tool to con-
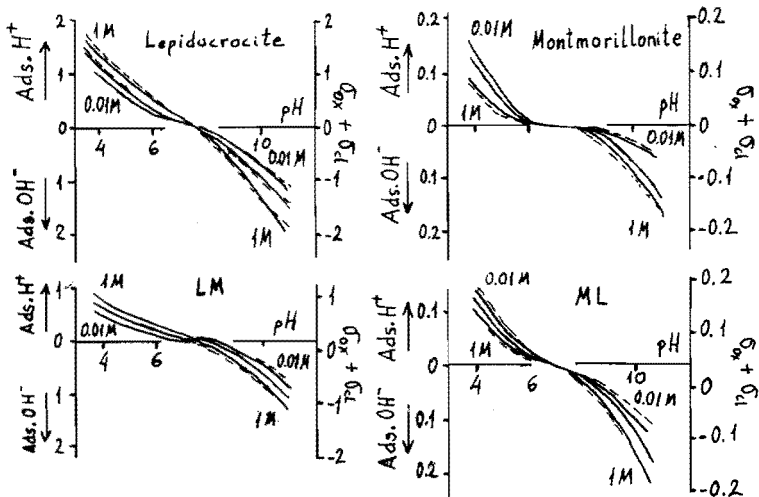
All ordinates are given in $eq.cm^{-2} \times 10^{10}$.

vert experimental ordinates to an absolute scale of $\sigma_{ox} + \sigma_{cl}$
when a crossover point is present. This is the case of the
curves for lepidocrocite, R=0, and sample LM, R=0.6 (60% of
the surface area of the mixture is calculated to correspond.
to montmorillonite). When R≠0, the correction term, $-\sigma_p R$,
must be included in the optimization routine of the compu-
ter program if σ_p is one of the adjustable parameters. When
R=0 the correction is obviously unnecessary.

For montmorillonite and ML, the crossover point no lon-
ger appears within the pH range studied, but there is an in
flexion point near the initial point of titration, where
the curves obtained at different ionic strengths run very
close to one another. A similar point of inflexion appears
in outputs of the model when R is close to 1 (data to be
published) and its ordinate is always $\simeq N_{ox}(1-R)$. The rea-
son for this behaviour of the model is not clear, but can
be used to convert the p.d.i. adsorption axis to $\sigma_{ox} + \sigma_{cl}$
when no crossover is apparent. For a pure clay, the $\sigma_{ox} + \sigma_{cl}$
values must be the same as those for p.d.i. adsorption, as

$1-R=0$. In the case of ML ($R=0.95$) the correction was also included in the program, as N_{ox} is one of the adjustable parameters.

The dashed lines show the results of the best fit of the model for each material (they are visible only in those regions where they can be distinguished from the experimental curves at the scale of the drawing). Pure lepidocrocite gave the values $N_{ox}=3\times10^{-9}$ eq.cm^{-2}, $G_{ox}=9\times10^{-13}$ eq.cm^{-2}.mV^{-1}, $G_d \simeq 1$, $K_{Hox}=1.2\times10^{8}$, $K_{OHox}=2.6\times10^{6}$, $K_+ =0.09$, $K_- =0.01$, and montmorillonite $N_{cl}=3.5\times10^{-11}$, $K_{Hcl}=2.0\times10^{3}$, $K_{OHcl}=8.0\times10^{3}$, $G_{cl}=10^{-8}$, $\sigma_p=-2.5\times10^{-11}$.The significance was high (P<0.01) in both cases.

The best fit for LM and ML gave very similar values of most parameters except N_{ox}, which resulted considerably smaller in both mixtures (1.9×10^{-10} for LM and 8.2×10^{-11} for ML). This unexpected result could suggest that the clay, with a much higher surface area than the oxide, interacts with the latter in such a way that it is able to block in a considerable degree the access of the adsorbing ions to the oxide. This assumption is supported by the fact that the value of N_{ox} is smaller the higher the value of R. More information is necessary to confirm this hypothesis, so that it should be taken carefully.

REFERENCES

Madrid, L. and Diaz-Barrientos, E. J. Soil Sci. (in press).

Sposito, G. 1984. The surface Chemistry of Soils. Oxford University Press.