



ADSORPTION OF MOLYBDATE BY CLAY MINERALS — II — MONTMORILLONITE AND ILLITE

The adsorption of molybdate by montmorillonite and illite was investigated at 25°C and 40°C in a 0.01 M sodium chloride background medium. A maximum of adsorption was observed at pH=3.8 for montmorillonite and at pH=4.0 for illite. Both clay minerals adsorb less molybdate at 40°C than at 25°C. The adsorption isotherms can all be fitted to the Langmuir equation. The limiting values are 1.98 mg Mo and 1.80 mg Mo per gram of montmorillonite at 25°C and 40°C, respectively; the corresponding values for illite are 0.424 mg Mo and 0.270 mg Mo per gram of adsorbent. The adsorption isotherms can be approached by straight lines and adsorption treated as a partition problem for molybdenum concentrations in solution lower than $0.2 \mu\text{g cm}^{-3}$ for montmorillonite and lower than $3 \mu\text{g cm}^{-3}$ for illite at 25°C, with K_d equal to $(15.3 \pm 1.6) \times 10^2 \text{ cm}^3 \text{ g}^{-1}$ for montmorillonite and equal to $(5.9 \pm 0.2) \text{ cm}^3 \text{ g}^{-1}$ for illite. Estimations of free energy, enthalpy and entropy of adsorption are presented for both clay minerals and for kaolinite as well.

1 — INTRODUCTION

The importance of molybdenum in agriculture and the determining role of clay minerals in the fixation and mobility of this element in soils have been reviewed in a previous publication [1].

Adsorption of molybdate by clay minerals is also interesting from the point of view of testing and comparing the performance of models which are currently being applied to the adsorption of ions by oxides, hydrous oxides and clay minerals [2-7]. Whereas a number of studies are available concerning another important nutrient, phosphate (*Cf.* ref. 2 and literature cited therein), data are relatively scarce for other specifically adsorbed anions. Adsorption of molybdate by oxides [8, 9, 10] and by clay minerals [8, 11] has been investigated but little information [12] seems to be available concerning its adsorption isotherms by clay minerals.

We have recently investigated the adsorption of molybdate by kaolinite [13]. In the present paper we report a similar study of the adsorption isotherms of molybdate by montmorillonite and illite at 25°C and at 40°C and also data on the 40°C isotherm for the system molybdate/kaolinite.

2 — EXPERIMENTAL

Montmorillonite was obtained from FLUKA. X-ray diffraction analysis of this material showed, besides the characteristic line of montmorillonite at 1.5 nm, a weak line at 1.0 nm indicating only a few per cent illite. Illite was obtained from CLAY MINERALS SOCIETY, SOURCE CLAY MINERALS REPOSITORY.

The X-ray pattern showed the two characteristic lines of illite at 0.496 nm and 1.0 nm; no other lines were observed thus indicating no contamination with other minerals.

Sedimentation analysis in hexametaphosphate medium yielded the particle size distri-

Table I

Particle size distribution for montmorillonite and illite

Mineral	> 50 μm	50-20 μm	20-2 μm	2-0.5 μm	< 0.5 μm
	(%)	(%)	(%)	(%)	(%)
Montmorillonite	12.6	10.3	44.7	21.0	9.9
Illite	17.0	24.1	28.9	17.0	11.4

bution shown in table I. Specific $\text{BET}_{(\text{N}_2)}$ areas are $220 \text{ m}^2 \text{ g}^{-1}$ and $21 \text{ m}^2 \text{ g}^{-1}$ for montmorillonite and for illite, respectively.

Preliminary experiments allowed to choose clay solution ratios equal to 10 g dm^{-3} for montmorillonite and to 50 g dm^{-3} for illite in order to obtain a conveniently measurable distribution of molybdate between solid and liquid phases. The initial Mo concentration ranged from 3 to $100 \mu\text{g cm}^{-3}$ for montmorillonite and from 1 to $250 \mu\text{g cm}^{-3}$ for illite. The initial pH of the suspensions in adsorption experiments was 4.0 for montmorillonite and 8.9 for illite, which were the pH the suspensions of these clays spontaneously assumed in 0.01 M NaCl medium.

Each adsorption equilibrium was carried out in three replicates. Equilibrium was reached in less than 24 hours in every case. In experiments at varying imposed pH, the suspensions were adjusted to the desired pH allowed to equilibrate overnight. The appropriate amount of molybdate solution was then added and the final pH measured after the exchange equilibrium was reached. The pH drift was always less than 0.8.

Experimental details concerning the equilibration procedure and the determination of molybdenum by flameless atomic absorption were given in a previous paper [13].

3 — RESULTS AND DISCUSSION

a) pH

The dependence of molybdenum adsorption on pH is shown in figures 1 and 2. A maximum is

reached at $\text{pH}=3.8$ for montmorillonite and at $\text{pH}=4.0$ for illite, both values being close to the pK_a of the HMoO_4^- as it could be anticipated from the theory of Hingston *et al* [14] and as we also observed in the case of kaolinite [13].

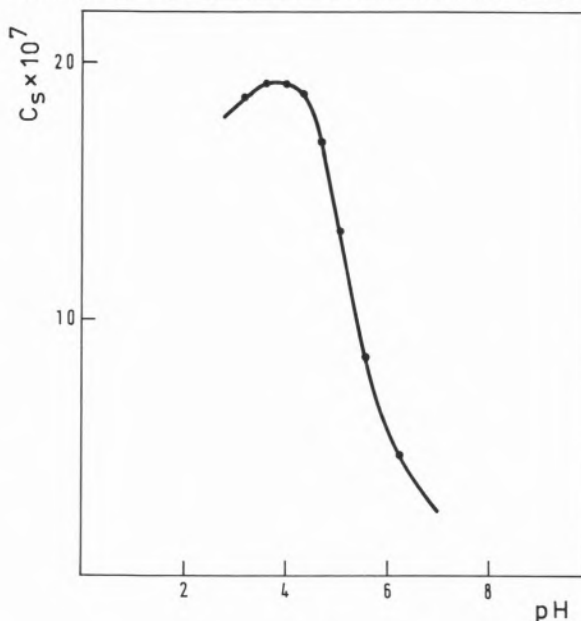


Figure 1

Adsorption of molybdate by montmorillonite: dependence on pH. 1 g montmorillonite; 100 cm^3 0.01 M NaCl; $\text{Co}(\text{Mo}) = 2.0 \text{ g cm}^{-3}$.

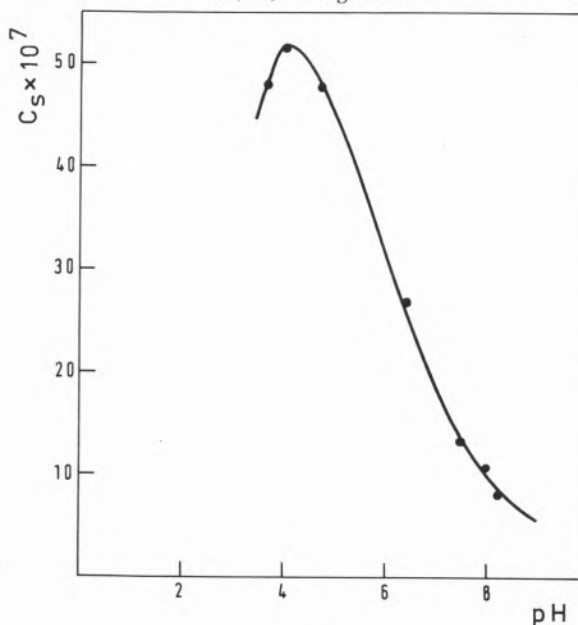


Figure 2

Adsorption of molybdate by illite: dependence on pH. 1 g illite; 100 cm^3 0.01 M NaCl; $\text{Co}(\text{Mo}) = 10 \text{ g cm}^{-3}$.

b) Molybdenum concentration. Temperature

Adsorption isotherms for montmorillonite and illite are shown in figures 3 and 4 for 25°C and 40°C respectively, pH remained unchan-

The four curves are all of L type (Giles classification [15]), molybdate showing less affinity for illite than for montmorillonite, and both minerals adsorbing less molybdate at 40°C than at 25°C.

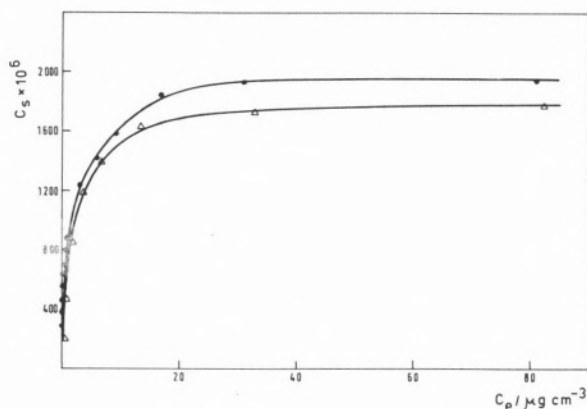


Figure 3

Adsorption isotherms for molybdate on montmorillonite in 0.01 M NaCl medium: ● 25°C (3.98 ≤ pH ≤ 4.05), Δ 40°C (3.85 ≤ pH ≤ 4.45)

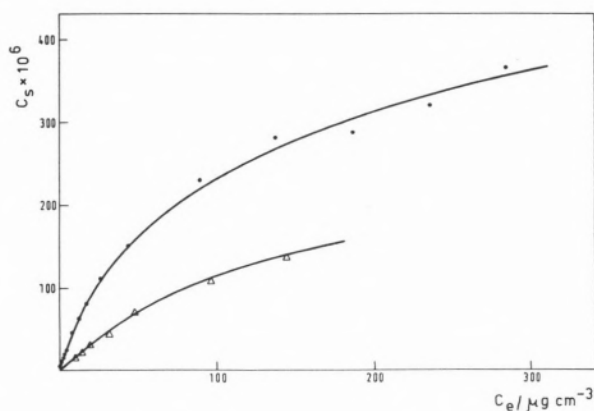


Figure 4

Adsorption isotherms for molybdate on illite in 0.01 M NaCl medium: ● 25°C (pH = 8.90), Δ 40°C (pH = 8.20)

ged during equilibration in the case of illite, owing to the buffering effect due to the high clay/solution ratio which was convenient to employ. As to montmorillonite, pH changed from 4.0 to at most 4.8 in the course of equilibration.

The isotherms at 25°C can be fitted to the Langmuir equation (Figs. 5 and 6), yielding for the linerarized form

$$\frac{C_e}{C_s} = 5.06 \times 10^{-4} C_e + 7.50 \times 10^{-4} \quad (1)$$

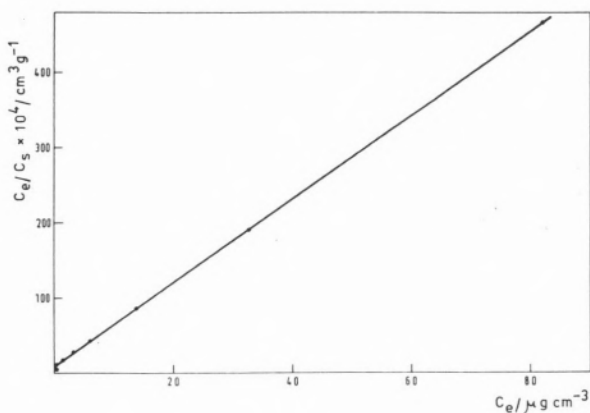


Figure 5

Langmuir plot for the adsorption isotherm of molybdate by montmorillonite at 25°C

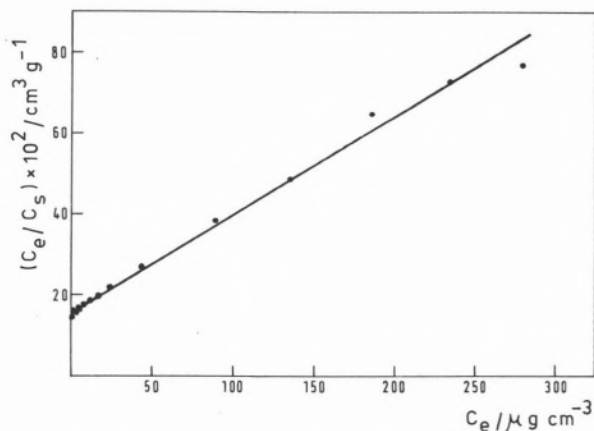


Figure 6

Langmuir plot for the adsorption isotherm of molybdate by illite at 25°C

for montmorillonite, and

$$\frac{C_e}{C_s} = 0.236 \times 10^{-2} C_e + 16.06 \times 10^{-2} \quad (2)$$

for illite, where C_e and C_s are the equilibrium Mo concentration in the liquid and solid phases expressed in $\mu\text{g cm}^{-3}$ and $\mu\text{g Mo g}^{-1}$ clay respectively.

The differences between calculated and experimental values amount to $9.4 \pm 3.2\%$ and to $4.4 \pm 0.9\%$ for montmorillonite and for illite respectively; these are to be compared with the variation coefficient for the experimental C_s , $2.2 \pm 0.3\%$. The fit is therefore reasonably good for illite but less so for montmorillonite. This may be connected with increasing affinity between molybdate and the adsorbent on going from illite to kaolinite and then to montmorillonite under our experimental conditions, namely an ionic strength of 0.01 M. Actually, all the isotherms being of L type, illite may nevertheless be considered to show some tendency to C-type behaviour and montmorillonite to H-type behaviour.

For molybdenum concentrations in solution lower than $0.2 \mu\text{g cm}^{-3}$ for montmorillonite and lower than $3 \mu\text{g cm}^{-3}$ for illite, the isotherms can be described by straight lines:

$$C_s = 15.3 \times 10^2 C_e \quad (C_e < 0.2 \mu\text{g cm}^{-3}) \quad (3)$$

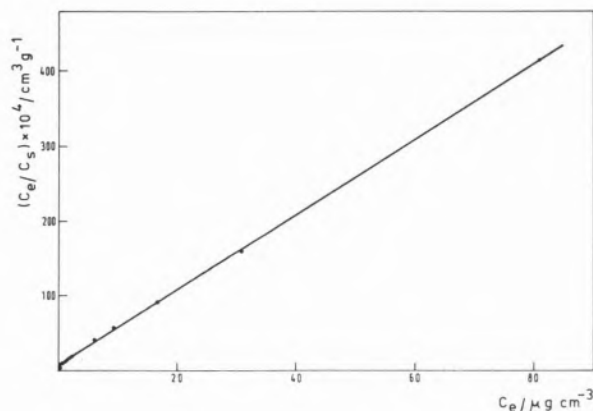


Figure 7

Langmuir plot for the adsorption isotherm of molybdate by montmorillonite at 40°C

for montmorillonite, and

$$C_s = 5.9 C_e \quad (C_e < 3 \mu\text{g cm}^{-3}) \quad (4)$$

The differences between calculated and experimental values amount to $8 \pm 3\%$ for montmorillonite and $4 \pm 2\%$ for illite. The adsorption equilibrium can thus be characterized in these concentration ranges by a single parameter, the distribution coefficient, K_d , which is equal to $(15.3 \pm 1.6) \times 10^2 \text{ cm}^3 \text{ g}^{-1}$ for montmorillonite and equal to $(5.9 \pm 0.2) \text{ cm}^3 \text{ g}^{-1}$ for illite.

Since molybdenum concentration in soil solution is typically lower than 3 ppm, adsorption of molybdenum by illite as a soil constituent can be treated as a simple partition problem. The same is true for kaolinite as we have shown in a previous paper [13]. As to montmorillonite, a two parameters equation, like Langmuir's, will be required in order to describe the behaviour of molybdenum in montmorillonitic soils.

The isotherms at 40°C can also be fitted to the Langmuir equation (Figs. 7 and 8) yielding for the linearized form

$$\frac{C_e}{C_s} = 5.57 \times 10^{-4} C_e + 7.99 \times 10^{-4} \quad (5)$$

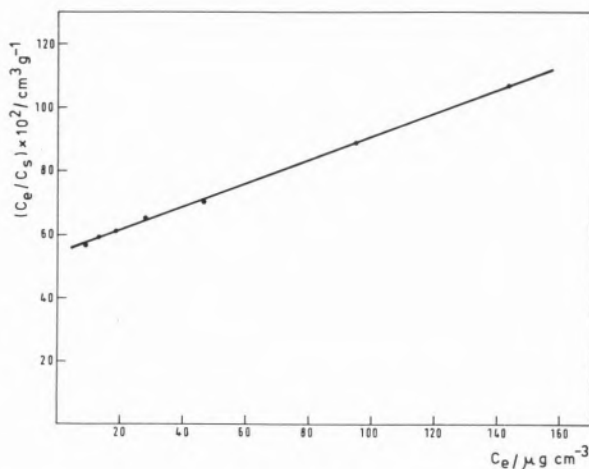


Figure 8

Langmuir plot for the adsorption isotherm of molybdate by illite at 40°C

for montmorillonite, and

$$\frac{C_e}{C_s} = 0.370 \times 10^{-2} C_e + 54.04 \times 10^{-2} \quad (6)$$

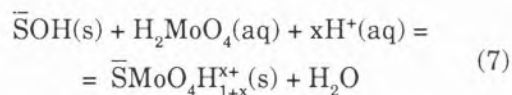
for illite. The differences between calculated and experimental values amount to $3.1 \pm 1.3\%$ and to $0.9 \pm 0.3\%$ for montmorillonite and illite respectively.

For low molybdenum concentrations the isotherms approach to straight lines as it was found at 25°C ; partition coefficients at 40°C are, however, unlikely to be useful in soil chemistry studies since this is not a common temperature in soils.

c) Equilibrium constants and thermodynamic functions

The fact that Langmuir equation adequately describes the adsorption equilibria we investigated makes it easy to advance preliminary estimation of the pertinent thermodynamic functions.

If speciation is ignored both in the liquid and the solid phases, the general stoichiometric equation can be put forward



corresponding to the conditional constant

$$K = \frac{C_s}{(C - C_s) C_e [\text{H}^+]^x} \quad (8)$$

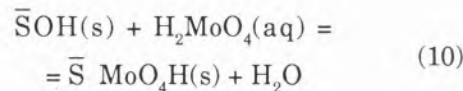
wherefrom the relationship

$$\frac{C_e [\text{H}^+]^x}{C_s} = \frac{1}{KC} + \frac{1}{C} C_e [\text{H}^+]^x \quad (9)$$

can be derived. (\bar{S} stands for one equivalent of the clay mineral and C for its exchange capacity for molybdate in the same units as C_s).

Now, whereas a good fit to equation (9) can be obtained with $x=0$, poor fitting resulted whenever stoichiometrically meaningful values of x ranging from $+2$ to -1 were tried. In any case, a systematically better agreement bet-

ween experimental and calculated values of C_s was observed when $x \rightarrow 0$. This suggests that equations (7) and (9) may be re-written as



and

$$\frac{C_e}{C_s} = \frac{1}{K_L C} + \frac{1}{C} C_e \quad (11)$$

equation (11) being the linearized form of Langmuir equation. The moderate increasing of pH which accompanies molybdate adsorption in the case of montmorillonite (and also kaolinite) should then be attributed to the readjustment of the acid-base equilibrium for the clay



upon the adsorption of molybdate, which consumes the SOH species. Potentiometric titrations of the clay suspensions corroborate this view.

Let it be pointed out that the Langmuir constant K_L is obtained from the extrapolation of the straight line (11) to the axis of ordinates: it therefore corresponds to an estimation of the equilibrium constant K for reaction (10) at zero Mo concentrations in both aqueous and solid phases. K_L may thus be taken as a fair approximation of the thermodynamic constant for the adsorption equilibrium. After conversion to molar concentration units for molybdenum in solution, it then refers to the following standard states under ideal conditions: unit molar concentration for molybdate in solution; and 0.5 mole fraction both for $\bar{\text{SOH}}(\text{s})$ and for $\bar{\text{SMoO}}_4\text{H}(\text{s})$.

The usual treatment of the equilibrium constants next yields the results that are summarized in table II, where data for kaolinite is also included for comparison.

Confidence intervals were estimated on the basis of the Langmuir fit, neglecting the cor-

Table II

Thermodynamic functions for the adsorption of molybdate by clay minerals

Function	Kaolinite	Montmorillonite	Illite
K(298K)	$(10.9 \pm 0.3) \times 10^3$	$(65 \pm 6) \times 10^3$	$(1.41 \pm 0.07) \times 10^3$
K(313K)	$(2.57 \pm 0.09) \times 10^3$	$(67 \pm 5) \times 10^3$	$(0.66 \pm 0.01) \times 10^3$
$\Delta G^\circ / \text{kJ.mol}^{-1}$	-23.0 ± 0.1	-27.4 ± 0.2	-18.0 ± 0.1
$\Delta H^\circ / \text{kJ.mol}^{-1}$	-75 ± 2	2 ± 2	-39 ± 1
$\Delta S^\circ / \text{kJ.mol}^{-1}.\text{K}^{-1}$	-174 ± 1	98 ± 2	-72 ± 1

relation of the errors in the ordinates and in the abscissae; a more rigorous calculation would be rather involved and probably unjustified. Precision confirms that estimates of ΔH° and ΔS° are possible and the results significant, even if only two temperatures were investigated. Accuracy, on the other hand, depend on how reliable the identification of K with K_L proves to be.

The driving force for the adsorption of molybdate by montmorillonite is of an entropic nature under our experimental conditions. The same has been found by Muljadi *at al.* [16] in the case of the adsorption of phosphate by kaolinite at pH = 5; the authors report zero enthalpy, -20 kJ.mol^{-1} free energy (at 20°C) and $+63 \text{ J.mol}^{-1}.\text{K}^{-1}$ standard entropy for the exchange reaction. The values shown in table II are of similar magnitude, with the exception of the entropy of adsorption of molybdate by kaolinite which may seem too high. However, if the adsorption of molybdate by kaolinite is to a certain extent assimilated to a bi-dimensional formation of aluminum molybdate (without significant simultaneous re-arrangement of exchangeable cations) the high entropy decrease is perhaps not surprising, if it is also born in mind that the standard entropy of formation of ferrous molybdate, for which data are available, is equal to $-335 \text{ J.mol}^{-1}.\text{K}^{-1}$ [17].

A more refined thermodynamic treatment, based on the use of the Gibbs-Duhem equation,

in order to obtain, from the conditional constants the thermodynamic equilibrium constants as well as the activity coefficients in the solid phases [18], depends on the confirmation of the stoichiometry of the adsorption reaction. This, on its turn, requires a detailed knowledge of the acid-base equilibria for the clays. The same is true if the adsorption equilibrium constants (and the thermodynamic functions) are to be derived from model considerations using, for instance, the constant capacitance model [2]. The acid-base behaviour of the clay minerals we have studied is therefore under investigation at present.

(Received 25th May 1986;
in revised version, 22nd September 1987)

ACKNOWLEDGEMENTS

The authors wish to thank Prof. Farinha Portela of the Instituto Superior Técnico de Lisboa for the BET area determination, Dr. Vieira e Silva of the Instituto Nacional de Investigação Agronómica, Oeiras, for the granulometric and X-ray diffraction analyses, and Prof. Remy Freire, Director of the Instituto Nacional de Investigação das Pescas, Lisboa, for the kind permission to utilise the flameless atomic absorption equipment and other facilities which made this investigation possible.

REFERENCES

- [1] M. M. MOTTA BATISTA and C. F. MIRANDA, *O Molibdénio nos Solos*, INIC, Lisboa (1981).
- [2] S. GOLDBERG and G. SPOSITO, *Soil Sci. Soc. Am. J.*, **48**, 772 (1984).
- [3] W. STUMM, R. KUMMERT and L. SIGG, *Croat. Chem. Acta*, **53**, 291 (1980).
- [4] J. WESTALL and H. HOHL, *Adv. Colloid Interface Sci.*, **12**, 265 (1980).
- [5] H. HOHL, L. SIGG and W. STUMM, In: M. C. Kavanaugh and J. O. Leckie (ed.) *Particulates in water*. Adv. Chem. Ser. n.º 189, p.l. Am. Chem. Soc., Washington DC (1980).
- [6] J. W. BOWDEN, S. NAGARAJAH, N. J. BARROW, A. M. POSNER and J. P. QUIRK, *Aust. J. Soil Res.*, **18**, 49 (1980).
- [7] P. W. Schindler, In: M. A. Anderson and A. J. Rubin (ed.) *Adsorption of inorganic at solid-liquid interfaces*, p.l. Ann Arbor Science, Ann Arbor, MI (1981).
- [8] L. H. P. JONES, *J. Soil Sci.*, **8**, 313 (1957).
- [9] E. D. REYES and J. J. JURINAK, *Soil Sci. Soc. Am. Proc.*, **31**, 637 (1967).
- [10] R. M. MCKENZIE, *Aust. J. Soil. Res.*, **21**, 505 (1983).
- [11] B. K. G. THENG, *N. Z. Sci.*, **14**, 1040 (1971).
- [12] P. J. PHELAN and S. W. MATTIGOD, *Clays Clay Miner.*, **32**, 45 (1984).
- [13] M. M. G. MOTTA and C. F. MIRANDA, *Rev. Port. Quím.*, **27**, 505 (1985).
- [14] F. J. HINGSTON, R. J. ATKINSON, A. M. POSNER and J. P. QUIRK, *Nature*, **275**, 1459 (1967); id. *Trans. 9th Int. Cong. Soil Sci.*, **1**, 669 (1968).
- [15] G. H. GILES, D. SMITH and A. HUITSON, *J. Colloid Interface Sci.*, **47**, 755 (1974).
- [16] D. MULJADI, A. M. POSNER and J. P. QUIRK, *J. Soil Sci.*, **17**, 238 (1966).
- [17] R. C. WEAST, *CRC Handbook of Chemistry and Physics*, CRC Press, Inc., Florida (1983), p. D76.
- [18] G. H. BOLT, In: G. H. Bolt and M. G. M. Bruggenwer (ed.) *Soil Chemistry. B. Physico-Chemical Models*, p. 27; Elsevier Scientific Publishing Company Amsterdam (1979).

RESUMO

Adsorção de molibdato por minerais de argila - II - montmorilonite e ilite

Estudou-se a adsorção de molibdato por montmorilonite e ilite a 25°C e a 40°C em meio de cloreto de sódio 0.01 M. Testou-se a influência do pH na adsorção tendo-se verificado um máximo a pH = 3.8 para a montmorilonite e a pH = 4.0 para a ilite. Ambos os minerais de argila adsorvem menos molibdato a 40°C do que a 25°C. As isotérmicas de adsorção ajustam-se bem à equação de Langmuir para os dois adsorventes e temperaturas. Os recobrimentos totais são respectivamente 1.98 e 1.80 mg Mo por grama de montmorilonite a 25°C e 40°C respectivamente; os correspondentes valores para a ilite são 0.424 e 0.270 mg Mo por grama de adsorvente.

Para concentrações de equilíbrio inferiores a 0.2 µg Mo cm⁻³ para a montmorilonite e a 3 µg Mo cm⁻³ para a ilite as isotérmicas de adsorção confundem-se com rectas podendo o equilíbrio ser tratado como um problema de partição e caracterizado por um coeficiente de distribuição K_d, igual a (15.3 ± 1.6) × 10² cm³ g⁻¹ para a montmorilonite e igual a (5.9 ± 0.2) cm³ g⁻¹ para a ilite. Apresentam-se estimativas dos valores da energia livre, entalpia e entropia de adsorção para os dois minerais de argila bem como para a caulinite.