ChemClass Journal, 2005, Volume 2, (41-44)

Isotherms for the adsorption of some quaternary amines from glycol solution unto α–goethite surface

---

A.F. Uzoamaka, A. Uzairu and G.F.S. Harrison*
Department of Chemistry , Ahmadu Bello University, Zaria, Nigeria

ABSTRACT

The isotherms for the adsorption of the quaternary ammonium salts – $(C_2H_5)_4N^+Cl^-$, $C_2H_5)_4N^+Br^-$, $(C_2H_5)_4N^+I^-$, $(NH_4)^+Cl^-$ and methylene blue from glycol solutions have been determined at 25, 30 and 35^0C. It has been suggested that some features of these isotherms might be understood on the basis of a reaction scheme that incorporates simple adsorption at the glycerol/FeOOH interface without cation or anion exchange.

*Author for correspondence

INTRODUCTION

The adsorption from aqueous solution of simple inorganic cations and anions onto goethite surface has been of some interest [1,2] and studies have shown that the most commonly exposed surfaces are the (100) – planes surfaces where we have hydroxyl groups classified as A, B and C. Surface oxide ions have also been identified and named C″ [3]. Thus the surface of this mineral is heterogeneous if the location of the hydroxyl groups and the surface oxygen anions are presumed to be the adsorption sites which, moreover, have been identified as of the Lewis-acid type and not of the Brönsted acid type [3].

With such a heterogeneous surface, adsorption from water/goethite interface has been found to be quite complicated and surface complexation, surface precipitation in both cation and anion adsorption have been postulated [4,5]:

$$FeOH + M^{2+} + H_2O \rightleftharpoons FeO{-}MOH_2^{+} + H^{+} \quad \text{..........(1)}$$

$$FeOH + A^{Z-} \rightleftharpoons A^{(Z-1)} + OH^{-} \quad \text{..........(2)}$$

$$FeOH + M^{2+} + 2H_2O \rightleftharpoons Fe(OH)_{3(s)} + MOH_2^{+} + H^{+} \quad \text{..........(3)}$$

(M^{2+} ≡ free cation; ≡ FeOH = surface hydroxyl site)

Obviously, water is a complicating solvent and the simple adsorption from the water/FeOOH would be obscured by many other surface interactions as we have seen. For this reason, it was thought that the adsorption of an ion and a cation from a less polar solvent than water might limit the number of strong surface interactions and so facilitate the adsorption on the goethite surface.

Glycerol was chosen as a solvent of compromise so as to allow for easily measurable solubility of the quaternary salts $(C_2H_5)_4N^+Cl^-$, $(C_2H_5)_4N^+Br^-$, $(C_2H_5)_4N^+I^-$, $(NH_4)^+Cl^-$ and methylene blue, the adsorbates.

EXPERIMENTAL

The goethite samples were prepared following the method of Atkinson *et al* [6]. Percentage purity determined as iron content was 96.5% (60.00±0.02% Fe). Particle sizes of samples were between 0.210 and 0.150 mm.

Except for methylene blue, adsorbate concentrations were determined as halide. Methylene blue concentrations were determined by the usual spectrophotometric method.

Apparatus

Adsorption was effected in the special apparatus whose diagram is shown in Fig. 1

RESULTS

The drop in concentration of solute in glycerol per unit mass of adsorbent has been plotted against the equilibrium concentrations of the solute for $(C_2H_5)_4N^+Cl^-$, $(C_2H_5)_4N^+Br^-$, $(C_2H_5)_4N^+I^-$ and $(NH_4)^+Cl^-$ and shown in Figs. 2-4. A similar plot for methylene blue is presented in Fig. 5.

$(NH_4)^+Cl^-$ and $(C_2H_5)_4N^+Cl^-$

The isotherms at 25^0C for ammonium chloride and tetraethyl ammonium chloride are similar with plateaux at 0.4 x 10^{-3} mol $dm^{-3}g^{-1}$ and 0.5 x 10^{-3} mol $dm^{-3}g^{-1}$ (adsorbate and presumable at the goethite/glycerol interface) respectively. By analogy with Langmuir type adsorption isotherms, the similarity heights of the plateaux suggest that the values of the equilibrium constants for the adsorption processes are close. Another similarity is seen at low concentrations where, apparently, there is no adsorption until equilibrium concentration is nearly 0.2 x 10^{-3} mol dm^{-3} for ammonium chloride and 0.15 x 10^{-3} mol dm^{-3} for the other adsorbate. At the higher temperatures of 30^{o}C there are apparently dramatic changes at these curves. At low concentration, there is no longer any 'delayed' adsorption and at higher concentration a maximum appears in each isotherm before the plateau. There is however, one difference and that is the large drop in the height of the plateau from 0.5 to 0.2 mol dm^{-3} g^{-1} for the quarternary salt but none at all for $(NH_4)^+Cl^-$ (at 30^0C). At 35^0C, the maximum disappears in both isotherms but the height of the plateux remains unchanged for $(NH_4)^+Cl^-$ and rises from 0.2 (at 30^0C) to 0.3 x 10^{-3} mol dm^{-3} g^{-1} for the other solute.

$(C_2H_5)_4N^+Br^-$

The isotherms for the bromide are similar to those of the quaternary chloride at 25 and 30^{o}C but the bromide, at 25^0C, apparently, has higher adsorption than the chloride and the plateau height is also greater for the former (bromide). Another difference in plateau height: for the bromide, this falls almost below the initial value of 0.1 x 10^{-3} mol dm^{-3} g^{-1} at 35^{o}C, the two isotherms differ considerably. The chloride curve does not show a 'maximum' in contrast with the bromide curve and at low concentrations the latter (bromide) shows 'delayed' adsorption but former does not. There is, however, one similarity and that is that the plateau height for both curves are the same (0.3 x 10^{-3} mol dm^{-3} g^{-1})

$(C_2H_5)_4N^+I^-$

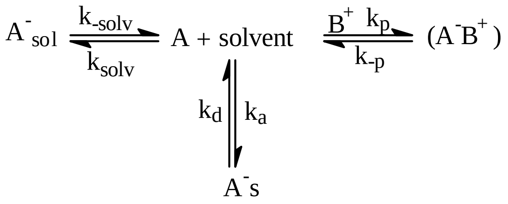
The iodide isotherms are completely different from those of the other quaternary salts and are best described as 'stepped' curves. However, the 'step' or plateau heights at 0.3 and 0.4 (25^{o}C); 0.2 and 0.3 (30^{o}C) and, 0.2, 0.3, 0.4 (35^{o}C) mol dm^{-3} g^{-1} are closer to those of the chloride than the bromide.

Methylene blue

The isotherm for methylene blue shows no resemblance to those of any of the other adsorbates in this series. For a start, equilibrium concentrations of the solute are several orders of magnitude lower than the rest and so are the values of the amounts adsorbed. At 25 and 30^{o}C there is an apparent 'kink' in the isotherms between ~ 0.1 and ~ 0.2 x 10^{-6} mol dm^{-3} equilibrium concentrations otherwise these, as well as, the 35^{o}C isotherms are nearly straight lines (with positive slopes) which merge at higher concentrations.

DISCUSSION

The discussion of these results already presented centres around the following feature of the isotherms: 'plateux', the adsorption at low and high concentrations of solutes and the apparent maximum in the isotherms. A reaction scheme for anions and cation interactions is proposed in order to guide these discussions.



Scheme I for anion (cation) interaction

The rate constants are indicated in the diagram. It is also to be noted that the surface complex A^-_s might be different for different adsorption sites.

We assume three different 'hydroxyl' adsorption sites - α, β, γ with $N_\alpha N_\beta N_\gamma$ number of sites for α, β and γ sites respectively. If the fraction of α, β and γ sites covered by the adsorbate are α, β and γ and the overall fractional coverage θ is given by:

$$\theta = \frac{N_\alpha \alpha}{N} + \frac{N_\beta \beta}{N} + \frac{N_\gamma \gamma}{N} + ... \quad (1)$$

$$N = N_\alpha + N_\beta + N_\gamma$$

It can be shown that for the proposed scheme

$$\theta = \frac{K_1 + K_2 c_{A^-} + K_3 c^2_{A^-}}{(1 + K_0 c_{A^-} + K'_2 c^2_A + K_3 c^3_{A^-})N} + \frac{(k_{-sov} c_{A^-} - k_{solv} c_{A^- solv})(1 + 2K_0 c_{A^-} + K'_2 C^2_{A^-})}{(1 + K_0 c_{A^-} + K'_2 C^2_{A^-} + K_3 c^3_{A^-})N} \quad ....(2)$$

$$+ \frac{(k_{-p} c_{A^-} c_{B^+} - k_p c_{A^- B^+})(1 + 2K_0 c_{A^-} + K'_2 C^2_{A^-})}{(1 + K_0 c_{A^-} + K'_2 C^2_{A^-} + K_3 c^3_{A^-})N}$$

The first expression in equation (2) is the adsorbate – adsorbent term and the first and second expressions may be taken as the solvation and ion – pair equilibria terms respectively. K_0, K_1, K_2, K'_2, K_3 are equilibrium constants defined as follows:

$K_0 \equiv K_\alpha + K_\beta + K_\gamma$
$K'_2 \equiv K_\alpha K_\alpha + K_\beta K_\beta + K_\gamma K_\gamma$
$K_3 \equiv K_\alpha K_\beta K_\gamma$
$K_1 \equiv K_\alpha N_\alpha + K_\beta N_\beta + K_\gamma N_\gamma$
$K_2 \equiv K_\alpha K_\beta (N_\alpha + N_\beta) + K_\beta K_\gamma (N_\beta + N_\gamma) + K_\alpha K_\gamma (N\alpha + N_\gamma)$

K_α, K_β, and K_γ are the equilibrium constants for the adsorption equilibrium at the sites α, β, γ.

We now consider two special cases

Case I:

$K_\alpha \approx {}_\beta \approx K_\gamma = K$;

Equation 2 then becomes

$$\theta = \frac{K + 2K^2 c_{A^-} + K^3 c_{A^-}^2 / N}{1 + 3Kc_{A^-} + 3K^2 c_{A^-}^2 + K^3 c_{A^-}^3} +$$

$$\frac{1}{N} \frac{1 + 6Kc_{A^-} + 3K^2 c_{A^-}^2}{1 + 3Kc_{A^-} + 3K^2 c_{A^-}^2 + K^3 c_{A^-}^3} \Big[k_{-solv} (c_{A^-} - K_p c_{A^- solv}) + k_{-p} \left(c_{A^- B^+} - K_p c_{A^- B^+} \right) \Big] \quad ....(3)$$

For large K (strong binding) 3K > 1 and at high equilibrium solute concentrations, first and zero order terms may be neglected, so that

$$\theta \cong \frac{K / N}{3 + Kc_{A^-}} + \frac{3}{N(3 + Kc_{A^-})} \begin{bmatrix} k_{-solv} \left(c_{A^-} - K_p c_{A^- solv} \right) + \\ k_{-p} \left(c_{A^- B^+} - K_p c_{A^- B^+} \right) \end{bmatrix} .....(4)$$

The form of the first term suggests that θ will decrease at high concentrations and even fall dramatically if ion-pair formation dominates, i.e.

$c_{A^-} << K_{solv} c_{A^- so;v}$ and $c_{A^- B^+} << K_p c_{A^-} c_{B^+}$

So that the last two terms become negative. In that case a peak in the curve might be expected at higher concentrations.

On the other hand, at low concentrations, second and higher order terms in c_A^- might be neglected so that;

$$\theta \approx K\left(\frac{1 + Kc_{A^-}}{1 + 3Kc_{A^-}}\right) + \left(\frac{1 + 6Kc_{A^-}}{1 + 3Kc_{A^-}}\right)[k_{-solv} (c_{A^-} - k_{solv} c_{A^- solv}) + k_{-p} (c_{A^- B^+} - K_p c_{A^-} c_{B^+})] \quad ....(5)$$

Ion – pair formation and solvation are unlikely to be important so that at sufficiently low concentration the first term in equation (5) might be dominant.

Now write the first term as

$$\frac{K}{1 + 3Kc_{A^-}} + \frac{K^2 c_{A^-}}{1 + 3Kc_{A^-}}$$

In a region of small equilibrium solute concentration such that $K >> 1 + 3Kc_{A^-}$ the second term is more important than the first and a slow rise in θ with increasing c_A^- might be expected at small c_A^-.

For weak binding i.e. K small, and at low concentration, c_A- is small. θ ≈ K if terms of order higher than zero are neglected. In this case, even ion – pair formation and solvation are unimportant. At high concentrations, the form of θ is hard to predict.

In summary, in the case of strong binding the isotherm may not have a plateau but a peak and at low concentrations, a flat curve. This fits in with the bromide isotherm at 35°C.

CASE II

An alternative case is if $N_\alpha \approx N_\beta \approx N_\gamma = N_0$

$$\theta \approx \left(\frac{N_0 K_0 + 2N_0 K'_2 c_{A^-} + K_3 c_{A^-}^3}{K_0 c_{A^-} + K'_2 c_{A^-}^2 + K_3 c_{A^-}^3} \right) / N + ...(6)$$

For sufficiently large N, we drop the last term in the numerator even if K_3 is large because of the coefficient K_3/N; if K_3 is large but K_0 and K'_2 are small, then for $K'_2 < K_0$, at high concentrations, drop the term containing K'_2 in the numerator, so that;

$$\theta \approx \left(\frac{K_0}{K_0 c_{A^-} + K'_2 c_{A^-}^2 + K_3 c_{A^-}^3} \right) x...... + ...(7)$$

The isotherm falls with increase in c_A- in the region. For small c_A-

$$\theta \approx \left(\frac{K_0 + 2K'_2 c_{A^-}}{1 + K_0 c_{A^-}} \right) x.......... + \quad ....(8)$$

If $K_0 >> 1$, then a linear isotherm with positive slope is possible in this region. The quaternary bromide and chloride at 30°C fit this model. The iodide and methylene blue isotherms would be discussed in a later publication.

REFERENCE

1. F. J. Hingston, A. M. Posner, and J. P. Quirk (1972). Anion Adsorption by Goethite and Gibbsite. I. The Role of the Proton in Determining Adsorption Envelopes. *J. Soil Sci.*, **23**: 177-192.

2. C. D. K. His and D. Langmuir (1985). Adsorption of Uranyl onto Ferric Oxyhydroxides: Application of the Site-Binding Model. *Geochem. Acta*, **49**: 1931-1941.
3. R. L. Parfitt, J. D. Russell and V. C. Farmar (1976). Confirmation of Surface Structure of Geothite (α-FeOOH) and Phosphate by Infrared Spectroscopy, *J. Chem. Soc*., *Faraday Trans*. I, **72**: 1082-1087.
4. L. Sigg and W. Stuum (1980). The Interaction of Anions and Weak Acids with Hydrous Geothite (α-FeOOH) Surface. *Colloids Surf*., **2**: 101-117.
5. D. E. Yates and T. M. Healey (1975). Mechanism of Anion Adsorption at Ferric and Chromic Oxides/Water Interfaces. *J. Colloid Interface Sci*., **52**: 222-228.
6. R. J. Atkinson, A. M. Posner and J. P. Quirk (1968). Crystal Nucleation in Fe (III) Solutions and Hydroxide Gels. *J. Inorg. Nucl. Chem*., **30**: 2371-2381.