THE FRONTIER BETWEEN ADSORPTION AND PRECIPITATION OF POLYACRYLIC ACID ON CALCIUM CARBONATE

C. GEFFROY, J. PERSELLO and A. FOISSY

Université de Franche-Comté[1]

B. CABANE

CEA Saclay[2]

F. TOURNILHAC

Rhône-Poulenc Recherche[3]

(1) Laboratoire d'Électrochimie et des systèmes dispersés,
16, route de Gray,
25030 Besançon Cedex - France

(2) 91190 Gif-sur-Yvette - France

(3) 93300 Aubervilliers - France

FRONTIÈRE ENTRE ADSORPTION ET PRÉCIPITATION DE L'ACIDE POLYACRYLIQUE SUR LE CARBONATE DE CALCIUM

L'adsorption des polymères sur les surfaces minérales qui permet de stabiliser une suspension colloïdale a des applications largement répandues dans les procédés industriels. Le mécanisme de liaison a été bien décrit sur les surfaces d'oxyde, principalement en termes de lien d'hydrogène et d'interactions électrostatiques entre sites chargés et segments de polymère. Ce phénomène a été mis en modèle et l'influence du pH, de la résistance ionique et du poids moléculaire peut être calculée ou prédite.

Dans le cas de substrats faiblement solubles tels que le $BaSO_4$, $CaCO_3$ ou $CaSO_4$, plusieurs problèmes apparaissent : la difficulté d'identifier les sites de surface et l'interférence des ions provenant de la solubilité du matériau. Dans le cas de la calcite, la solubilité induit des ions calcium dissous dans la solution, ce qui peut complexer le polyélectrolyte et réduire sa solubilité.

Dans ce but, nous avons mesuré l'énergie de liaison en utilisant la microcalorimétrie. Les mesures microcalorimétriques ont montré que l'enthalpie d'adsorption est faiblement endothermique : environ 2 kJ/mol. Il est intéressant de noter que cette valeur est très proche de celle de la complexion du calcium avec PANa. Il est suggéré que la force d'entraînement pour l'adsorption est le gain net en entropie du système. L'isotherme d'adsorption microcalorimétrique ne montre aucune évidence d'une interaction fortement exothermique entre les bords positifs et les segments négatifs du polyion.

Pratiquement, dans la plupart des cas, l'adsorption des polymères est calculée à partir de la diminution de sa concentration dans la solution après séparation du solide par centrifugation. Cette procédure ne distingue cependant pas l'adsorption réelle et la séparation des phases.

Pour répondre à la question, nous avons réalisé des expériences d'adsorption en utilisant une membrane de dialyse pour séparer les particules solides de la solution. Il a été établi que dans certaines circonstances, dépendant de la quantité relative de calcite, des ions calcium et du polyélectrolyte, une précipitation a lieu plutôt qu'une adsorption. Ceci est spécialement le cas pour les faibles concentrations de polymères (moins de 2 g/l).

Les isothermes d'adsorption ont été correctement reproduits en prenant en compte tout l'équilibre de la solution, y compris les constantes d'association du calcium et du sodium et une limite de solubilité pour le complexe calcium-polymère. Ce dernier a été

déterminé par titrage turbidimétrique pour différents poids moléculaires du polymère.

Notre conclusion est qu'en présence d'ions divalents, ce qui est souvent le cas avec des minéraux difficilement solubles, la liaison surface/polyélectrolyte provient d'un phénomène de précipitation plutôt que d'un phénomène d'adsorption.

THE FRONTIER BETWEEN ADSORPTION AND PRECIPITATION OF POLYACRYLIC ACID ON CALCIUM CARBONATE

Adsorption of polymers on mineral surfaces allowing colloidal stability have widespread applications in industrial processes. The binding mechanism has been quite well described on oxide surfaces. Mainly in terms of hydrogen bonds and electrostatic interactions between charged sites and polymer segments. This phenomenon has been modelized and the influence of pH. Ionic strentgh, and molecular weight can be calculated or predicted.

In the case of sparingly soluble substrates such as $BaSO_4$, $CaCO_3$ or $CaSO_4$, several problems arise: the difficulty for the identification of surface sites and the interference of ions coming from the material's solubility. In the case of calcite, the solubility imposes dissolved calcium ions in solution which could complex the polyelectrolyte and reduce its solubility.

For that purpose, we have measured the binding energy using microcalorimetry. Microcalorimetric measurements have shown that the adsorption enthalpy is weakly endothermic: about + 2 kj/mol. Interestingly, this value is very closed to that of calcium complexation with PANa. It is suggested that the driving force for adsorption is the net gain in entropy of the system. The microcalorimetric adsorption isotherm does not show any evidence for a strongly exothermic interaction between positive edges and negative segment of the polyion.

Practically, in most cases, adsorption of polymers is calculated from the decrease of its concentration in the solution after separation of the solid by centrifugation. This procedure does not discriminate therefore between real adsorption and phase separation.

To answer the question, we have performed adsorption experiments using a dialysis membrane to separate the solid particles from the solution. It has been established that in some circumstances, depending on the relative amount of calcite, calcium ions and polyelectrolyte, precipitation takes place rather than adsorption. This is especially the case at low polymer concentration (less than 2 g/l).

Adsorption isotherms were correctly reproduced, taking into account all solution equilibria, including calcium and sodium binding constants and a solubility limit for the calcium polymer complex: the latter was determined by turbidimetric titration for various polymer molecular weights.

Our conclusion is that in the presence of divalent ions which is often the case with sparingly soluble minerals, the surface binding of the polyelectrolyte results from a precipitation rather than an adsorption phenomenon.

FRONTERA ENTRE LA ADSORCIÓN Y PRECIPITACIÓN DEL ÁCIDO POLIACRÍLICO SOBRE EL CARBONATO DE CALCIO

La adsorción de los polímeros en las superficies minerales, que permite estabilizar una suspensión coloidal, tiene aplicaciones ampliamente conocidas en los procedimientos industriales. El mecanismo de enlace ha sido ya correctamente descrito sobre las superficies de óxido, principalmente en términos de vínculo de hidrógeno y de interacciones electrostáticas entre emplazamientos cargados y segmentos de polímero. Este fenómeno se ha podido poner en forma de modelo y la influencia del pH, de la resistencia iónica y el peso molecular se pueden ya calcular o predecir.

En el caso de substratos de baja concentración en cuanto a su solubilidad, como por ejemplo el $BaSO_4$, $CaCO_3$ o el $CaSO_4$, se presentan varios problemas: la dificultad para identificar los emplazamientos de superficie y la interferencia de los iones procedentes de la solubilidad del material. En el caso de la calcita, la solubilidad induce iones de calcio disueltos en la solución, lo cual puede llegar a complejar el polielectrolito y reducir su solubilidad.

Con este objeto, hemos procedido a la medición de la energía de enlace utilizando la microcalorimetría. Las mediciones microcalorimétricas han venido a demostrar que la entalpia de adsorción es de bajo grado endotérmico: aproximadamente 2 kJ/mol. Resulta interesante tener en cuenta que este valor está muy cercano de aquel de la complexión del calcio con PANa. Se sugiere así que la fuerza de arrastre por la adsorción representa la ganancia neta en entropia del sistema. El isotermo de adsorción microcalorimétrico no muestra ninguna evidencia de interacción ampliamente exotérmica entre los bordes positivos y los segmentos negativos del poli-ión.

Prácticamente, y en la mayor parte de los casos la adsorción de los polímeros se calcula tomando como punto de partida la disminución de su concentación en la solución tras separación del sólido por centrifugación. Este procedimiento no establece, no obstante, la distinción entre la adsorción real y la separación de las fases.

Para responder a esta cuestión, hemos llevado a cabo experiencias de adsorción, utilizando una membrana de diálisis para separar las particulas sólidas de la solución. Se ha llegado a establecer que, en ciertas circunstancias, que dependen de la calidad relativa de la calcita, los iones de calcio y el polielectrolito, tiene lugar una precipitación mejor aún que una adsorción. Este es el caso, especialmente, para las concentraciones reducidas de polímeros (menos de 2 g/l).

Las isotermas de adsorción se han reproducido correctamente teniendo siempre en cuenta la totalidad del equilibrio de la solución, e inclusive las constantes de asociación del calcio y del sodio y un límite de solubilidad para el complejo calcio-polímero. Este último, se ha determinado por titulación turbidimétrica para distintos pesos moleculares de polímeros.

Llegamos así a la conclusión por la cual, en presencia de iones divalentes, cosa que ocurre frecuentemente cuando se trata de minerales difícilmente solubles, el enlace superficie/polielectrolito procede de un fenómeno de precipitación, mejor aún que de un fenómeno de adsorción.

INTRODUCTION

Adsorption of polyelectrolytes on mineral surfaces has been already investigated by several authors and quite well modelled in the case of opposed or uncharged surface. We have worked on a negatively charged sodium polyacrylate that is assumed to be a good model for weak polyelectrolyte. Its charge has been found to increase with the pH, the apparent acidic pK being around pH = 4,7 (Dupont, 1995).

In the adsorption process, one has to consider that two types of interaction exist between the substrate and its adsorbate (Klein): these called "specific" that include adsorption on particularly reactive sites are mainly electrostatic and the non specific interactions including all hydrophobic effects, Van der Waals forces, entropy and desolvation considerations.

For oxide surfaces, that are considered as homogeneous, typical descriptions of the interface have been made in term of electrostatic interactions, hydrogen bond and hydrophobic forces (Böhmer, Van der Schee). The oxide surface is described as formed by M-OH sites that can ionise themselves in the water as a function of the pH of the medium and the intrinsic point of zero charge of the material. Apparition of $M-O^-$ or $M-OH_2^+$ sites will lead to electrostatic interactions between the mineral and the polyelectrolyte (Gebhardt). An usual assumption is to consider that the polymer chain has many points of contact with the surface called trains (that are not necessarily successive segments of the chain), the part between two trains are called loops and the chain' end protruding in the solution are tails. The influence of the ionic strength and the molecular weight have been quite well understood and predictions of Fleer's model are at least semi quantitatively good (Evers).

Concerning non oxide mineral such as clay or mineral substrate, the difficulty arises from the description of the surface (adsorption) sites. Speciation can be made when the studied mineral has a reasonably high specific area and a relatively low solubility: for instance, basal and neutral faces have already been identified at the montmorillonite surface. When the mineral is soluble, the precipitation and recristallisation phenomena that are likely to occur with quick kinetic rate are limiting the investigation methods. That lead to the registration of conflicting reports about the calcite-water interface for the last few years even on the sign of the surface charge! All to day,

only crystallographic information available from X-ray, EXAFS and MEB measurements seem to satisfactorily inform on the structure of the soluble mineral surfaces (Van der Leeden).

Moreover, in the case of $CaCO_3$, $CaSO_4$ and $BaSO_4$ that are known to be sparingly soluble minerals, another interfering phenomenon has to be taken into account. The solubility of these material enable them to act as infinite sources of divalent ions. That effect has certainly to be considered in the adsorption process.

In fact, divalent cations are known to act on the charge of the mineral surface (they may create positive adsorption sites), on the bulk conformation of the polymer chain and its solubility, and at last on the range of electrostatic forces drastically decreasing with increasing the ion (and especially divalent) concentration.

Our work consists with the identification of the adsorption mechanism. To our knowledge, three possible mechanisms have been proposed:

- a specific adsorption on remaining positively charged sites at the mineral surface originating from hard electrostatic attraction and leading to a great negative enthalpy of displacement (Van der Leeden);

- a specific electrostatic interaction between a negatively charged surface site and a positive segment of the polymer temporarily complexed by a calcium ion (Dupont, 1993);

- a non specific sticking mechanism arising from the solubility loss of the polymer complexed by the calcium in the bulk or at the solid-liquid interface (Ringenbach).

Unfortunately, no report on the separation of these two phenomena that are adsorption on sites and precipitation due to the loss of solubility of the polyelectrolyte has been found.

We have tried to distinguish between H bond formation and precipitation of polyacrylic acid at increasing neutralisation rates. These experiments permit us a better understanding of the base carbonate role and showed the importance of the ratio calcium on sodium. The calcium is effectively responsible for the phase separation of the polymer. In the case of fully ionised sodium polyacrylate where no acid-base reaction is supposed to occur, we have tried to assess the amount of precipitated polyacrylate by an original dialysis experiment.

1 EXPERIMENTS

1.1 Adsorption as a function of α

The adsorption of polyacrylic acid onto a mineral surface may be understood in terms of H bond as proposed by Fleer in the case of uncharged polymer on silica particles.

This assumption is however reliable when no additional bulk reaction occurs. In the case of calcite, the role of the carbonate base can not be neglected. In fact, adsorption on a calcite suspension can be considered as an acid base reaction between the protons of the polyacid and the carbonate ions dissolved in solution by the mineral. This affirmation is supported by the fact that the adsorbed amount increases linearly in a great range of polyacrylate concentration and reaches a coverage rate that seems to be unrealistic excluding a multilayer precipitation process (Fig. 1).

Figure 1

Precipitation of PAAH onto $CaCO_3$.

Beside of it, the carbonate particle are sticking one to another and are quite hydrophobic allowing a quick phase separation (<1 minute). Comparison of the adsorption isotherm at $\alpha = 0$ and $\alpha = 1$ shows some great differences that we have tried to make clear by varying the rate of neutralisation of the polyacrylate.

Increasing α will lead to many simultaneous effects:

- increase of the segment-segment repulsion;
- increase of the electrostatic attraction with positively charged sites and repulsion with the negatively charged ones;
- increase of the segment-solvent parameter, it means greater solubility of the chain.

The adsorption in function of α is shown hereafter (Fig. 2).

We have also reported the final transmittance of the suspension after 5 minutes of sedimentation and the electrophoretic mobility of the particles. It is clear that a minimum amount of sodium is necessary for a good dispersing effect of the polyacrylate. This quantity is around one sodium for one proton. In fact, the presence of sodium on the polymer chain ensures the electrostatic repulsion between same charged bodies.

The decrease of the electrophoretic mobility changing from $+2$ to -2 is understood as a balance between the positive surface and the more negatively charged sodium polyacrylate adsorbed in the interface. The isoelectric point of the calcite is around pH $= 8.4$ and the decrease of the adsorbed amount could be attributed to the increase of the repulsion between charged groups, the surface remaining positively charged. Moreover the final pH of the suspension is constant for α going from 0 to 0.4.

This denotes the buffering effect of the carbonate ions. The principle acid-base reactions occurring in our system are schematised on Graph 1.

One may note two smashing effects when increasing α:

- the electrophoretic mobility of the particles remains constant whereas the amount of sodium present on the polymer chain is hardly increasing;
- the adsorbed amount does not decrease drastically whereas segmental repulsion increases and electrostatical attraction decreases.
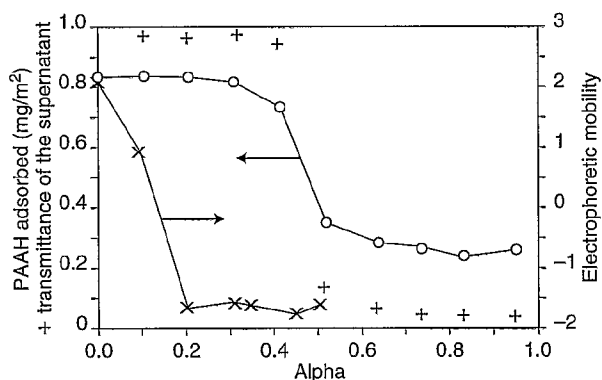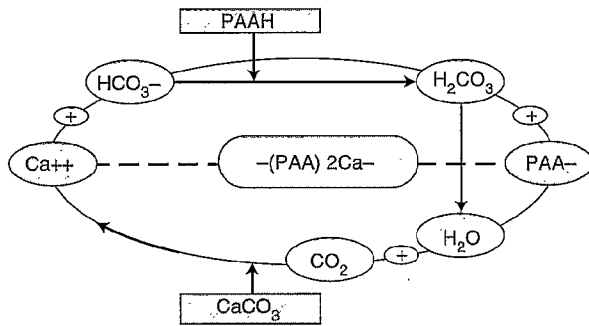

Figure 2

PAAH adsorption vs its neutralisation rate.

Graph 1

Role of the carbonate ions in the precipitation process.

These two points suggest that a bulk reaction may occur simultaneously and that the ratio calcium on sodium is of importance in the understanding of the adsorption mechanism.

1.2 Adsorption of sodium polyacrylate

The adsorption of sodium polyacrylate is known to decrease with the increase of the pH (Fig. 3). The final pH monitored after adsorption is always higher that the initial one: It accounts for displacement of the carbonate ions from the surface or in the bulk, all the case induced by calcium complexation.
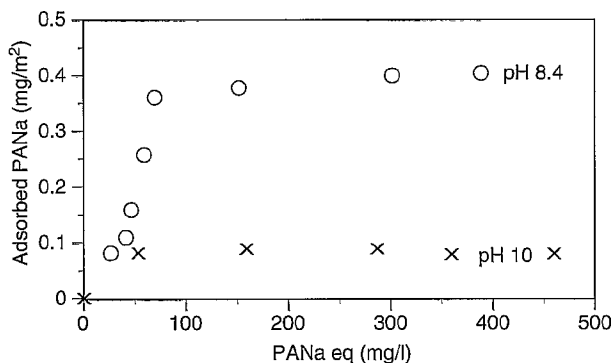
With increasing the pH of the bulk, it is assumed that two concomitant phenomena compete:

- the increase of the negative surface charge of the calcite particles that can ensure hard electrostatic repelling between the polymer and the surface;
- the decrease of the amount of calcium ions in the bulk that are able to reduce the solubility of the polymer or enhance Van Der Waals attraction.

We tried to separate these two influences of the pH by adding calcium ions into the medium. After addition of calcium chloride, we have followed the evolution of the adsorbed amount of two sodium polyacrylate: one has a molecular weight of 60.000 and can precipitate easily in a poor solvent, the other of molecular weight equal to 2100 does not become hydrophobic before high calcium concentrations. The experiments were made at the same pH = 9, ratio Solid/Volume (that has been found to be of importance: Adam) and initial polymer concentration. Moreover, we inverted the order of addition of the components of our sytem, it means first adding calcium to the polymer solution. In that case, one cannot invoke a surface site creation induced by the calcium ions. However, we found the same values as in the first case: a distribution of the calcium ions between the surface and the polymer is put forward.

The curves show that the behaviour of the polyacrylate is highly dependant on its molecular weight. It is suggested that the polymer of high molecular weight precipitate when the ratio calcium on segment is near 0.37,

Figure 3

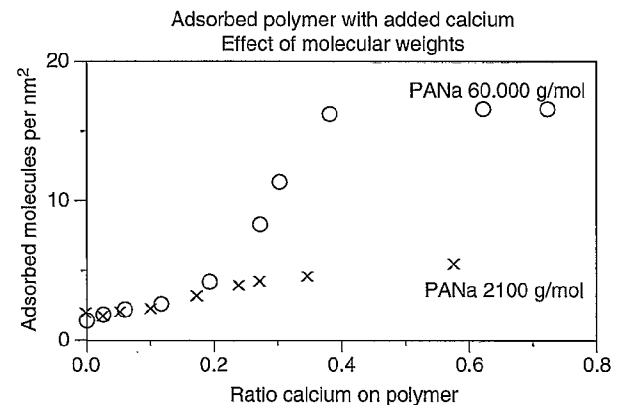Adsorbed PANa as a function of the initial pH of the suspension.

Figure 4

Adsorption of two PANa in the presence of multivalent ions.

that has already been proposed by Jarnström and Dupont. The interesting points of these curves are threefold:

- First of all, the phase separation of the polymer begins whereas the ratio calcium on polymer reaches 0.2. That means that the calcite is able to liberate many calcium ions (proportionally to the concentration of the polymer).

- Secondly, the beginning of the high adsorption does not fit with the change in zeta potential induced by specific adsorption of calcium ions onto the surface.

- For the 2100, the increase of the adsorbed amount is quite linear. We can propose this plausible explanation: the added calcium gradually reduces the electrostatic repulsion between the polymer coil (complexed or bare) and the globally negative calcite surface. It induces a greater affinity of the polymer for the surface via a quite hydrophobic effect.

It is suggested that the polymer could be bound non specifically onto the surface for entropic reasons. This type of mechanism has been proposed by Norde in the case of protein where the conformation of the molecule is the driving force of the adsorption process that does not vary from positively to negatively charged substrate.

1.3 Binding enthalpy of PANa onto calcite

We have investigated this binding enthalpy by microcalorimetry on a Tian Calvet microcalorimeter already described in the literature (Partyka). The total recorded enthalpy is the sum of the dilution enthalpy and the displacement enthalpy. The dilution enthalpy measured by diluting a polymer solution into water at a fixed ionic strength is found to be negligible. The evaluation of the binding enthalpy of the molecule toward the surface has been found to be positive, it means endothermic:

As a result, we have compared the adsorption enthalpy of polyacrylate per mole of adsorbed segment with that of complexation with a saturated solution of calcium carbonate. These two values have been found to be of the same order of magnitude and about +2 kJ/mole. That endothermic value and the fast kinetic of adsorption confirms that the mechanism is entropy driven. In fact, writing $DG = DH - TDS$, DG being negative, a positive value of the enthalpy must be accompanied by a net gain in entropy of the system.

This positive value suggests a desolvation either of the surface or of the ions during the adsorption process. In order to make it clear, we have measured the adsorption enthalpy at various amount of surface available (Fig. 5).

No linear correlation has been found between the quantity of surface and the displacement enthalpy. This would lead credence to the assumption that a non specific interaction exists between the polymer and the surface, arising from a bulk reaction. In fact, this bulk reaction of complexation of the calcium with the carboxylate segment is accompanied by a desolvation of the calcium and a rehydration of the counter ion surrounding the carboxylate functions displaced by the chemical reaction. Hence, it would be of great interest to quantify the bulk contribution in the adsorption process.
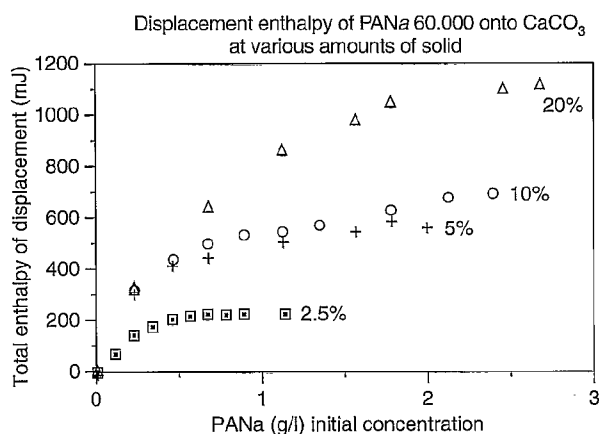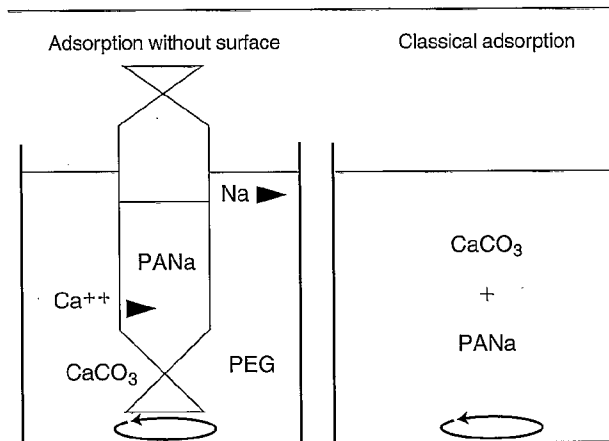

Figure 5

Displacement enthalpy at various amount of surface.

1.4 Adsorption without surface

Practically, the adsorbed amount is merely determined by a difference between the initial and the final amount of polymer at the equilibrium, therefore not discriminating the specific adsorption from the precipitation. We have tried to assess the amount of complexed polyacrylate during the adsorption by preventing it to be in contact with the surface. For that purpose we have used a dialysis membrane between the calcite suspension and the polyacrylate solution at various initial concentrations, the two solutions being first equilibrated at the same pH value.

The scheme of our dialysis experiment is shown hereafter (Graph 2): we have called it adsorption without surface in order to compare our results with the adsorption isotherm at the same pH.

Graph 2

Scheme of the dialysis experiment.

Figure 6

Kinetic of the dialysis experiment.

Figure 7

Comparison between adsorption and precipitation.

This dialysis experiment will be termed when the chemical potential of the water and of the ions will be the same in the two parts of the membrane. In order to avoid dilution effects due to the differential osmotic pressure, various amounts of polyethylene glycol (Mw = 35 000) are dissolved in the calcium carbonate suspension. This polymer is supposed to let the dissolution rate of the calcite quite unchanged. The kinetic of our experiment is controlled by checking the conductivity of the solution in the membrane (Fig. 6). It can be seen that the equilibrium state takes a long time. Hence, the system is allowed to evoluate during a month and the inner and outer volume are checked just after the end.

The trouble polymer solutions are then centrifuged and the amount of disappeared polyacrylate is expressed as a function of its initial concentration.

Referring to Figure 7, it has been found that the first points of the adsorption isotherm are due to precipitation of the polyacrylate. This precipitate has been analysed in terms of calcium and sodium concentration and about 5% (mol) of sodium have been found. These measurements are in agreements with the increasing zeta potential and in the sodium balance made apart.
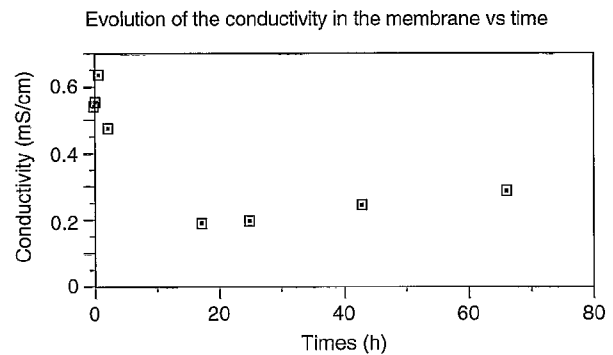
However, the good fit of our precipitation values is reliable till small concentrations in the order of 1 g/l. In fact, the polymer solution remains clear with increasing its concentration.

Practically, it has been possible to determine the amount of calcium liberated by the calcite in the presence of sodium polyacrylate (Fig. 8). One can observe that a quasi plateau is obtained: it has been explained by the increasing amount of carbonate ions, enhancing the pH value and avoiding calcite dissolution. Thus, the increase in polyacrylate concentration will lead to more calcium dissolved but less complexated polymer (the ratio calcium on polymer decreases). Unfortunately, we can't determine if the calcium polyacrylate is precipitated at the calcite surface or if a phase separation occurs. Out of it, SANS experiments will certainly make clear this point.
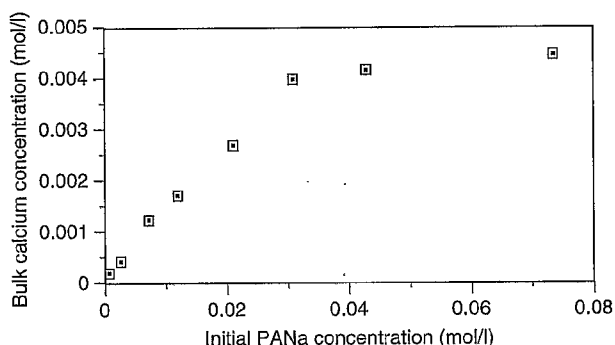
Figure 8

Calcite dissolution forced by PANa. Closed vessel.

This is strong evidence that a neutralisation-precipitation process occurs in the interface but is simultaneously accompanied by a real specific adsorption on sites that have to be clearly identified and quantified.

CONCLUSION

This work suggests that the consideration of bulk reaction cannot be neglected in the case of soluble material. It has already been proposed by Laskowski that the precipitation process could be of importance in the displacement of the point of zero charge of materials via adsorption. In our case, there is strong evidence that the adsorption process is very complex: depending on the net gain in entropy of the system and on the competition of surface and bulk reactions. We have showed the importance of the calcium in the solution, and we propose that the adsorption process could be now considered as a non specific interaction between the polymer and the surface. We have also shown that precipitation could be mistaken with site adsorption. In fact, site adsorption should really occur at high polymer concentration where no interfering bulk reactions

can be put forward. These types of sites are however supposed to be very few as supported by the enthalpy measurements.

Our actual work consists of the identification of these surface sites that are supposed to be few and highly depending on the chemistry of the adsorbant.

ACKNOWLEDGEMENTS

REFERENCES

Adam U.S. and I.D. Robb (1983), *J. Chem. Soc.*, Faraday Trans. I, **79**, pp. 2745-2753.

Böhmer M.R., O.A. Evers and J.M.H.M. Scheutjens (1989), *Macromolecules*, **23**, pp. 2288-2301.

Dupont L., A. Foissy, R. Mercier and B. Mottet (1993), *Journal of Colloid and Interface Science*, **161**, pp. 455-464.

Dupont L. and A. Foissy (1995), *Colloids and Surfaces*, A: **110**, pp. 235-248.

Evers O.A., G.J. Fleer, J.M.H.M. Scheutjens and J. Lyklema (1985), *Journal of Colloid and Interface Science*, **111**, pp. 446-454.

Gebhardt J.E. and D.W. Fuerstenau (1983), *Colloids Surf*, **7**, p. 221.

Klein J. (1985), *Journal of Colloid and Interface Science*, **111**, pp. 305-313.

Laskowski J.S. (1993), *Journal of Colloid and Interface Science*, **159**, pp. 349-353.

Norde W., F. Macritchie, G. Nowicka and J. Lyklema (1985), *Journal of Colloid and Interface Science*, **112**, pp. 447-456.

Partyka S., M. Lindheimer, S. Zaini, E. Keh and B. Brun (1985), *Langmuir*, **2**, pp.101-105.

Ringenbach E., G. Chauveteau and E. Pefferkorn (1995), *Journal of Colloid and Interface Science*, **171**, pp. 218-223.

Stenius P., L. Järnström and M. Rigdahl (1990), *Colloids and Surfaces*, **51**, pp. 219-238.

Van der Schee H.A. and J. Lyklema (1984), *J. Phys. Chem*, **88**, pp. 6661-6667.

Van der Leeden M.C. and G.M. Van Rosmalen (1995), *Journal of Colloid and Interf. Science*, **171**, pp. 142-149.