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The Inhibiting Effect of Scandium Ions upon the Dissolution of Calcium Carbonate

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The purpose of this work has been to investigate the inhibiting action of small amounts of Sc^{3+} ions upon the dissolution of calcite in water saturated with CO_2. By carrying out experiments with radioactive ^{46}Sc as a tracer it was found that the rate of dissolution could be described by the empirical equation

$$\frac{dC}{dt} = k' \, (C_{real}^* - C) - k'' \, \overline{C}_{Sc^{3+}}$$

where C is the concentration of $Ca(HCO_3)_2$, t is the time, C_{real}^* is the solubility of $Ca(HCO_3)_2$, $\overline{C}_{Sc^{3+}}$ is the amount of Sc^{3+} adsorbed on the calcite surface, and k' and k'' are constants.

Based on the empirical equation, an explanation of the mechanism of inhibition during dissolution is suggested. The mechanism is supposed to be that Ca^{2+} and Sc^{3+} ions from the solution are adsorbed at active spots or "kinks" on the surface of the dissolving crystal, each adsorbed ion blocking the process of dissolution at one "kink".

Kinetics of the dissolution of calcite. The kinetics of the reaction defined by eqn. (1)

$$CaCO_3(s) + CO_2(g) + H_2O(l) \rightleftharpoons 2\,HCO_3^-(l) + Ca^{2+}(l) \qquad (1)$$

have been investigated by Erga and Terjesen [1] and by Terjesen, Erga, Thorsen and Ve.[2]

Their method was to blow CO_2 through an agitated aqueous suspension of calcite particles in a baffled vessel under such conditions that the aqueous phase was saturated with CO_2. The calcite particles were made from natural limestone of high purity. To obtain reproducible results it was found necessary to stabilize the reactivity of the calcite particles by a complex pretreatment with water saturated with CO_2 and containing small quantities of

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EDTA to remove impurities present as metal ions. Detailed informations concerning apparatus, preparation of calcite particles and experimental procedure are given in a previous paper.[2]

The negligible effect of the stirrer speed indicated that the rate of dissolution was determined by reactions taking place on the surface of the solid particles or in the stagnant liquid layer close to it. Calculation of theoretical rates of mass transfer confirmed this conclusion.

Several metal ions added to the solution in concentrations ranging from 10^{-3} to 10^{-7} M were found to inhibit the dissolution process. The effect increased with decreasing solubility of the corresponding metal carbonate. It was conjectured that similar effects were to be expected in other dissolving systems where the rate of dissolution was not controlled by mass transfer alone. Later experiments with CaF_2 have confirmed the general character of this phenomenon.[3,4]

In the presence of inhibitors the rate of dissolution was found to decrease linearly with increasing concentration of $Ca(HCO_3)_2$ to become essentially zero at an apparent equilibrium concentration lower than the solubility of $Ca(HCO_3)_2$. The experimental results could be described by a semi-empirical, first order eqn. (2)

$$\frac{\mathrm{d}C}{\mathrm{d}t} = k'\left(C_{\mathrm{real}}^* - C\,\frac{C_{\mathrm{real}}^*}{C_{\mathrm{app}}^*}\right) \quad (2)$$

where C_{real}^* and C_{app}^* represent real and apparent equilibrium concentrations of $Ca(HCO_3)_2$. The apparent equilibrium concentration decreases with increasing concentration of inhibitor in the solution.

For concentrations higher than the apparent equilibrium concentration eqn. (2) predicts negative rates of dissolution. It is obviously not applicable in this region.

As the rate of dissolution is controlled by reactions at the surface of the solid particles, knowledge of the adsorbed amount of inhibitor rather than its bulk concentration is essential to studies of the mechanism of inhibition. It should be noted that the surface concentration of inhibitor is likely to vary greatly during any particular experiment, and that the lack of accurate adsorption measurements greatly limits the value of the results earlier published.[1,2]

It is the purpose of the present work to determine surface concentrations of inhibitor and to use these as a basis for correlating rates of dissolution. For this purpose Sc^{3+} was chosen as an inhibitor. A number of experiments had already been carried out with these ions and the radioactive isotope ^{46}Sc is very convenient as a tracer. ^{46}Sc has previously been used in a similar experimental program to investigate the effects of inhibitors upon the dissolution of CaF_2.[4]

Both the surface concentration of inhibitor and the rate of dissolution are likely to vary along the surface of a particle and the resulting correlations will necessarily have to be overall correlations.

Adsorption of ions on calcite. Canals, Marignon and Cordier[5] examined polarographically the adsorption of Cu^{2+} and Zn^{2+} from dilute solutions.

Görlich and Görlich [6a] and Görlich, Görlich and Szwaja [6b] measured chromatographically the adsorption of several metal-ions. They found that the ions formed heavily soluble oxides and basic carbonates on the surface of solid calcite. Douglas and Walker [7] determined the adsorption by measuring the zeta-potential of Iceland spar against several metal chloride solutions. These results, however, are not directly applicable to our systems because they were carried out with solutions containing little or no CO_2. In the dissolution experiments on the other hand, the liquid was saturated with CO_2. CO_2 and pH are known to have profound effects on the adsorption equilibria. No adsorption measurements relating to solutions saturated with CO_2 could be found in the literature.

Inhibition of dissolution processes. It is generally accepted that the surface of a crystal of arbitrary shape consists of planes separated by ledges of monomolecular height, the ledges being broken by kinks at irregular intervals.

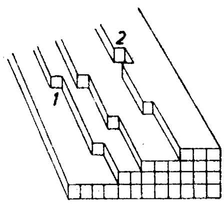

Fig. 1. The surface of a cubic crystal, showing [100]-planes, ledges and kinks (1, 2).

Fig. 1 schematically shows the surface of a cubic crystal. The dissolution of a crystal will then consist of three steps:

1. Formation of a kink.
2. Movement of a kink along a ledge.
3. Transportation of dissolved atoms from the surface to the bulk of the solution.

In recent years, the inhibiting effect of Fe^{3+} ions upon the etching of LiF crystals by various etchants has been extensively studied. Gilman, Johnston and Sears [8] found that 2.1×10^{-5} M Fe^{3+} ion reduced the rate of dissolution of LiF by a factor of 10, the reduction being more pronounced in the {100} direction than in the {110} and {111} directions. The authors concluded that the inhibition was caused by adsorption of Fe^{3+} ions at the kinks of type 1 on Fig. 1. Forming a strong complex with the F^- ions, the inhibiting ions were in this position forming a barrier to the movement of kinks along the ledges. Based upon the work of Gilman *et al.*,[8] Ives has published several papers on the same subject. A review of his results is given.[9] He measured the rate of widening of etch pits and found that the rate approached zero at a concentration of LiF much lower than its solubility at the prevailing experimental conditions. This observation clearly corresponds to the apparent equilibrium earlier found in the calcite experiments.[1,2] Adsorption of Fe^{3+} ions, containing the radioactive isotope ^{59}Fe, on {100} surfaces of LiF from its saturated solution showed that the adsorption was independent of macroscopic surface morphology. From a solution containing 3.6×10^{-5} moles of Fe^{3+} ions per litre, approximately 0.6×10^{-10} moles of Fe^{3+} ions per square centimetre of LiF were adsorbed. This corresponds to 1/35 of a monolayer. The adsorbed ions will then be about 6 sites apart in a square array. This distance fits well with the average spacing between monomolecular ledges on etch pit sides. Ives [9] considers double kinks of the type 2 on Fig. 1 to be the most likely sites of adsorption. According to Ives,[10] the main action of an inhibitor is to reduce the rate of movement of kinks whereas the rate of formation of kinks appears to be governed chiefly by the undersaturation of the dissolving material. The two effects are, however, not independent.

The results obtained by dissolving CaF_2 in water in presence of Sc^{3+} indicate that the reduction in rate of dissolution caused by the inhibitor is proportional to the number of inhibitor ions adsorbed per unit area of the fluorite surface.[4]

EXPERIMENTAL

Dissolution of calcite. The conditions of the previous experiments [2] with Sc^{3+} were reproduced in close detail with calcite from the same source. The surface concentration of Sc^{3+} was measured by using the radioactive isotope ^{46}Sc as a tracer.

Isotopic measurements. ^{46}Sc has a half-life of 84 days.[11] The material used in the experiments was prepared from spectrally pure $ScCl_3 \cdot 6H_2O$, manufactured by Johnson, Matthey & Co., Ltd., London. It was subjected to a flux of 10^{12} neutrons cm^{-2} sec^{-1} for 133 h in the reactor JEEP of The Norwegian Atomic Energy Establishment (IFA) at Kjeller. A gamma-spectre of the activated material showed no contamination from other radioactive isotopes. After dissolution in distilled water the concentration of Sc^{3+} was determined by titration with EDTA according to a procedure described by Welcher.[12]

The radioactive samples from the experiments were placed in small cylindrical test-tubes fitting the well of a 2″ × 1 3/4″ thallium-activated NaI crystal, type C.P., manufactured by Quartz & Silice, Paris. The crystal was attached to a F. H. 421 A scintillation counter and mounted in a lead tower. The counting was done with a F. H. 90 scaler and a F. H. 526 electric watch, this equipment was manufactured by Frieseke & Hoepfner, Erlangen.

Procedure. The experimental procedure for the dissolution was the same as previously described.[2] For the determination of Sc^{3+} small samples of the suspension were sucked off with a pipette and distributed between two test-tubes, a mixture of particles and solution in one and pure solution in the other. By a procedure of weighing and drying this arrangement made it possible to correct the radioactivity of the particles for the error arising from the Sc^{3+} contained in the solution clinging to them.

RESULTS

Kinetic measurements. The first experiments were designed to test the reproducibility of the technique, particularly the pretreatment mentioned earlier. The results of a reference experiment without inhibitor are shown in Fig. 2 and are seen to agree well with previous observations. For the material in question the real equilibrium concentration was 9.00×10^{-3} M $Ca(HCO_3)_2$, and k' in eqn. (2) was 9.07×10^{-3} per minute. The results obtained with 10^{-6} M $ScCl_3$ are also in excellent agreement with those of Ref. 2. (It should be noted, however, that the concentrations of $ScCl_3$ given in Ref. 2 were subject to an error and should be multiplied by 0.51.).

The series of experiments represented on Fig. 2 were carried out with varying amounts of $ScCl_3$ and started with particles not previously exposed to Sc^{3+} ions. The rate of dissolution was calculated by graphical differentiation of smooth curves fitted to the points on Fig. 2, but not shown on the figure. The values obtained were corrected for variations in calcite area per unit volume of solution caused by partial dissolution of the particles and removal of samples. Fig. 3 shows the corrected values of the rate of dissolution.

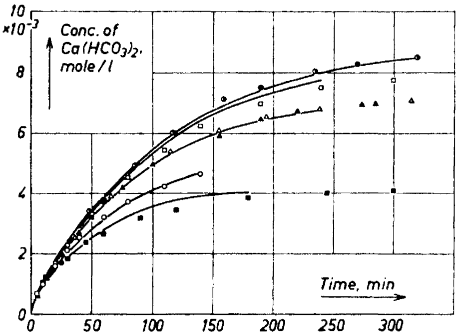

Fig. 2. The points represent the measured values of the concentrations of $Ca(HCO_3)_2$. The lines are obtained by integration of eqn. (3). ● Expt. No. 1. No $ScCl_3$ added. ◐ From Ref. 2. No $ScCl_3$ added. □ Expt. No. 2. 0.49×10^{-7} M $ScCl_3$. ▲ Expt. No. 3. 0.51×10^{-6} M $ScCl_3$. △ From Ref. 2. 0.52×10^{-6} M $ScCl_3$. ○ Expt. No. 4, part 1. 0.28×10^{-5} M $ScCl_3$. ■ Expt. No. 5. 0.52×10^{-5} M $ScCl_3$.

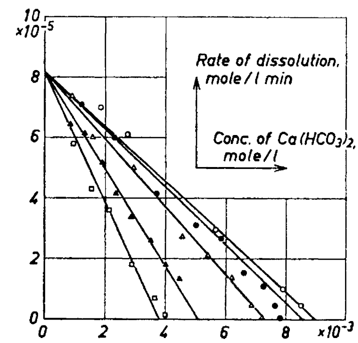

Fig. 3. The rate of dissolution as a function of the concentration of $Ca(HCO_3)_2$. ○ Expt. No. 1. No $ScCl_3$ added. ● Expt. No. 2. 0.49×10^{-7} M $ScCl_3$. △ Expt. No. 3. 0.51×10^{-6} M $ScCl_3$. ▲ Expt. No. 4, part 1. 0.28×10^{-5} M $ScCl_3$. □ Expt. No. 5. 0.52×10^{-5} M $ScCl_3$.

It was the intention of the present investigation to seek a correlation between the rate of dissolution, the surface concentration of inhibitor and the bulk concentration of $Ca(HCO_3)_2$. It was consequently of interest to carry out experiments with surface concentrations of the inhibitor which were not related to its bulk concentration. This was possible because, as will be shown later, the adsorption and desorption of the inhibitor were slow processes which never reached equilibrium. The results of such experiments are shown in Fig. 4. The first part of experiment No. 4, shown on Fig. 4, was interrupted after 140 min. 5 litres of the solution were then removed by decantation, and substituted by 5 litres of distilled water at 25°C, saturated with CO_2. Part 2 of the experiment was interrupted after further 200 min, and a similar operation carried out before part 3 was started. Experiment No. 7, shown on the same figure, was started with particles given a pretreatment with a diluted $ScCl_3$ solution corresponding to the ordinary pre-treatment with EDTA. All $ScCl_3$ introduced in this experiment was then adsorbed on the dry particles

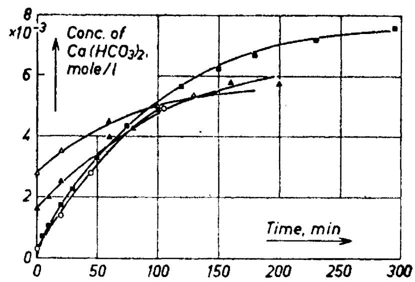

Fig. 4. The points represent the measured values of the concentrations of $Ca(HCO_3)_2$. The lines are obtained by integration of eqn. (3). ○ Expt. No. 6. 0.49×10^{-6} M $ScCl_3$. The moment when introduction of CO_2 was started is selected as starting point. ■ Expt. No. 7. Particles pre-treated with $ScCl_3$. △ Expt. No. 4, part 2. ▲ Expt. No. 4, part 3. The moment when the first sample after the introduction of fresh water was taken is selected as starting point in part 2 and part 3.

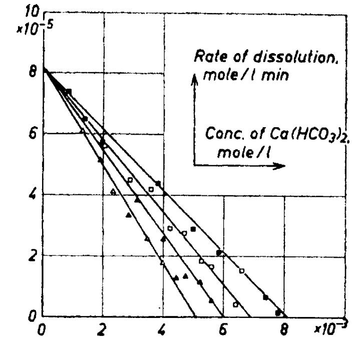

Fig. 5. The rate of dissolution as a function of the concentration of $Ca(HCO_3)_2$. △ Expt. No. 4, part 1. 0.28×10^{-5} M $ScCl_3$. ▲ Expt. No. 4, part 2. Particles from part 1. □ Expt. No. 4, part 3. Particles from part 2. ■ Expt. No. 7. Particles pretreated with Sc^{3+}.

before the dissolution started. Corrected data for the rate of dissolution of experiments Nos. 4 and 7 are plotted on Fig. 5.

Adsorption of inhibitor. The surface concentration of adsorbed inhibitor is expressed as moles of Sc^{3+} per square centimetre of calcite surface, and plotted on Figs. 6 and 7 as a function of the concentration of $Ca(HCO_3)_2$ for the dissolution experiments.

The greatest surface concentration of inhibitor measured was 4.90×10^{-10} moles of Sc^{3+} per square centimetre of calcite surface at 4.96×10^{-3} moles of $Ca(HCO_3)_2$ per litre.

Experiment No. 8 was started with a solution of $Ca(HCO_3)_2$ at its real equilibrium concentration, an analysis showed 8.99×10^{-3} M. The surface concentration of Sc^{3+} is plotted as a function of time on Fig. 8 where a corresponding plot of the results from experiment No. 3 is shown as a comparison.

Experiment No. 6 was started with CO_2-free water and $ScCl_3$. Due to adsorption on the walls of the stainless steel vessel, the concentration of Sc^{3+} in the solution dropped to approximately 50 % of its initial value after 80 min. At that time the calcite particles were introduced, and a strong adsorption of Sc^{3+} to the particles took place. After 330 min the CO_2 was introduced, and the surface concentration of Sc^{3+} on the particles dropped rapidly as shown on Fig. 6. The concentration of Sc^{3+} in the solution rose at the same time, mainly due to desorption from the vessel walls. At higher concentrations of $Ca(HCO_3)_2$ the surface concentration of Sc^{3+} on the particles rose slowly

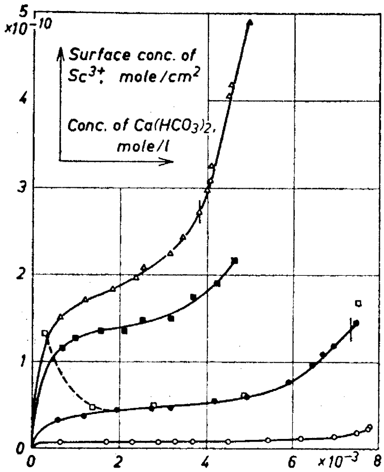

Fig. 6. The surface concentration of Sc^{3+} as a function of the concentration of $Ca(HCO_3)_2$. The vertical marks on the curves representing expts. Nos. 3 and 5 indicate the apparent equilibrium concentrations. ○ Expt. No. 2. 0.49×10^{-7} M Sc^{3+}. ● Expt. No. 3. 0.51×10^{-6} M Sc^{3+}. ■ Expt. No. 4, part 1. 0.28×10^{-5} M Sc^{3+}. △ Expt. No. 5. 0.52×10^{-5} M Sc^{3+}. □ Expt. No. 6. 0.49×10^{-6} M Sc^{3+}. The CO_2 was introduced after 330 min.

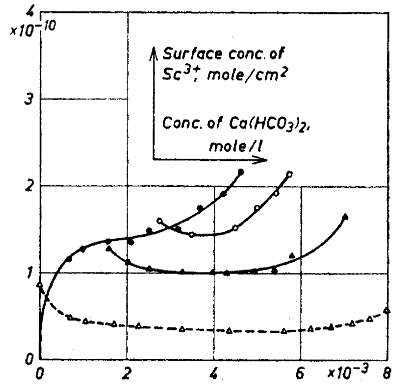

Fig. 7. The surface concentration of Sc^{3+} as a function of the concentration of $Ca(HCO_3)_2$. ● Expt. No. 4, part 1. 0.28×10^{-5} M Sc^{3+}. ○ Expt. No. 4, part 2. Particles from part 1. ▲ Expt. No. 4, part 3. Particles from part 2. △ Expt. No. 7. Particles pre-treated with Sc^{3+}, no Sc^{3+} added to the solution.

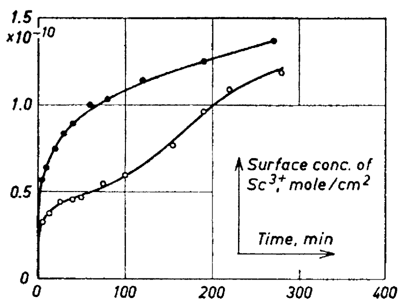

Fig. 8. The surface concentration of Sc^{3+} as a function of time. ○ Expt. No. 3. 0.51×10^{-6} M Sc^{3+}. ● Expt. No. 8. 0.48×10^{-6} M Sc^{3+}. The concentration of $Ca(HCO_3)_2$ was 8.99×10^{-3} M at $t=0$ min.

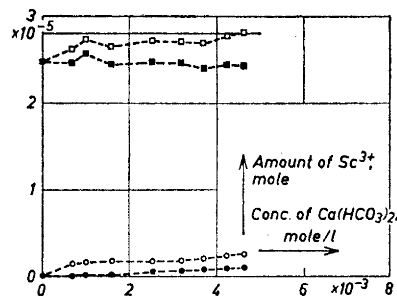

Fig. 9. Material balances for Sc^{3+} during expt. No. 4, part 1. 2.8×10^{-5} moles of Sc^{3+} were added. ● Amount of Sc^{3+} removed with samples. ○ Amount of Sc^{3+} adsorbed on the particles. ■ Amount of Sc^{3+} in the solution. □ Amount of Sc^{3+} accounted for by the measurements.

again. Fig. 6 shows the points to coincide well with those representing experiment No. 3. As the experimental conditions are identical except for the initial part of the experiments, this shows the reproducibility of the adsorption experiments.

A material balance on Sc^{3+} gives another control on the reliability of the measurements. Fig. 9 shows Sc^{3+} balances for experiment No. 4 at different concentrations of $Ca(HCO_3)_2$.

Washing 70 g of calcite-particles 10 times with 0.5 litres of water, free from CO_2, reduced the surface concentration of inhibitor slightly from 1.90×10^{-10} to 1.75×10^{-10} moles per square centimetre of calcite.

DISCUSSION

Analysis of the results. Experiment No. 8, see Fig. 8, where no destruction of the particle surface due to dissolution took place, clearly shows that the adsorption of Sc^{3+} on calcite is a comparatively slow process. The surface concentration of Sc^{3+} approaches no definite equilibrium value during the period examined. The higher rates of adsorption in experiment No. 8 as compared with experiment No. 3 is mainly caused by the increase in pH of a solution of $Ca(HCO_3)_2$ with increasing concentration. This point is clearly understood from consideration of Fig. 6. At the time of introduction of CO_2, the pH of the solution, then containing 2.9×10^{-4} M $Ca(HCO_3)_2$, had the value of 9. Introduction of CO_2 rapidly lowered the pH which in solutions containing 0.5×10^{-3} and 4×10^{-3} M $Ca(HCO_3)_2$ is 4.8 and 5.6, respectively. This sudden drop in pH rapidly reduced the amounts of Sc^{3+} adsorbed on the calcite particles. The dependence of the adsorption on pH also agrees well with the observations of Görlich *et al.*[6a,b]

The fully drawn curves on Fig. 6 all reveal the same characteristic shape, the flat part of the curves being less pronounced at higher concentrations of $ScCl_3$. The amount of Sc^{3+} adsorbed shows no trend towards approaching an equilibrium value. As indicated by the vertical marks on the curves representing experiments Nos. 3 and 5, there is no tendency towards desorption of inhibitor at concentrations higher than the apparent equilibrium. In the development of the preliminary theory of inhibition,[2] it was necessary to postulate such desorption in order to avoid violating the laws of thermodynamics. This theory will therefore require modification.

The Sc^{3+} adsorbed covers only a minor fraction of the calcite surface, 1.4×10^{-10} moles of Sc^{3+} per square centimetre corresponding to a coverage of about 1 %. The amounts of inhibitor adsorbed are of the same magnitude as measured by Ives [9] with LiF and Fe^{3+} ions and by the authors [4] with CaF_2 and Sc^{3+}. Considering experiment No. 3 at 1.4×10^{-10} moles of Sc^{3+} per square centimetre, 28.5 % of the Sc^{3+} present in the system are adsorbed on the calcite particles. The difficulties in washing the adsorbed Sc^{3+} from the particles with water indicate that the inhibitor is adsorbed on the surface of the calcite and not in the electrolytic double-layer.

The purpose of experiments Nos. 4 and 7 was to test the hypothesis that the rate of dissolution is not influenced by the way in which adsorption takes place. Fitting the results from these experiments into a general correlation between rate of dissolution, concentration of $Ca(HCO_3)_2$ and adsorbed amount of inhibitor will give an important support to this hypothesis.

Correlation of the results. It is possible, by combining Fig. 3 with Fig. 6 and Fig. 5 with Fig. 7, to plot the rate of dissolution as a function of the surface concentration of Sc^{3+}. This is done on Fig. 10, using the concentration

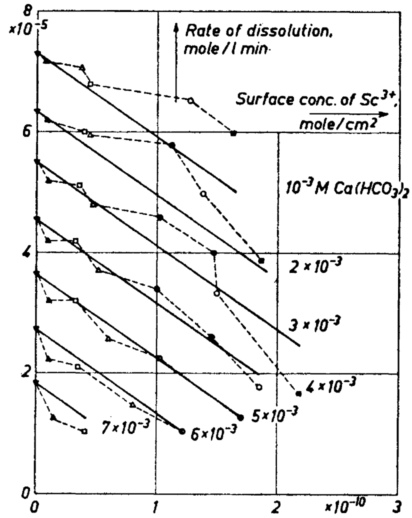

Fig. 10. The rate of dissolution plotted as a function of the surface concentration of Sc^{3+}. The dotted lines are drawn through points representing the same concentrations of $Ca(HCO_3)_2$. The fully drawn lines represent eqn. (3). ▼ Expt. No. 1. No Sc^{3+} added. ▲ Expt. No. 2. 0.49×10^{-7} M Sc^{3+}. □ Expt. No. 7. Particles pre-treated with Sc^{3+}. △ Expt. No. 3. 0.51×10^{-6} M Sc^{3+}. ◐ Expt. No. 4, part 3. Particles from part 2. ● Expt. No. 4, part 2. Particles from part 1. ○ Expt. No. 4, part 1. 0.28×10^{-5} M Sc^{3+}. ■ Expt. No. 5. 0.52×10^{-5} M Sc^{3+}.

of $Ca(HCO_3)_2$ as a parameter. There is a clear tendency for the points referring to the same concentration of $Ca(HCO_3)_2$ to group along straight, parallel lines. At low concentrations of $Ca(HCO_3)_2$, the values of the rate of dissolution and of the adsorbed amount of inhibitor are not very reliable. This is due to the high rates of dissolution and adsorption and may explain the deviations from straight lines at these concentrations.

The points plotted along the ordinate on Fig. 10 represent the rate of dissolution of the uninhibited reaction, experiment No. 1. The significance of the straight, parallel lines starting at these points is that the reduction in the rate of dissolution caused by inhibition is proportional to the number of Sc^{3+} ions per unit area of calcite. These parallel lines correspond to a rate equation of the form

$$\mathrm{d}C/\mathrm{d}t = k'\ (C_{\mathrm{real}}{*}-C)-k''\ \overline{C}_{\mathrm{Inh}} \qquad (3)$$

instead of the previous eqn. (2). $\overline{C}_{\mathrm{Inh}}$ denotes the surface concentration of Sc^{3+}. The value of the constant k'' may be calculated for each of the points plotted on Fig. 10 by a rearrangement of eqn. (3). The arithmetic mean of the calculated single values of k'' is in the actual units 1.51×10^{-5}, determining the slope of the parallel lines on Fig. 10. Values referring to 10^{-3} M $Ca(HCO_3)_2$ are excluded from the calculations for reasons explained above. Further more, experiment No. 2 is excluded because the low levels of radioactivity measured in this experiment give inaccurate values for the amounts of Sc^{3+} adsorbed.

To test the validity of eqn. (3), corresponding values of bulk concentration of $Ca(HCO_3)_2$ and surface concentration of Sc^{3+} have been inserted for each experiment and the corresponding values of the time, t, calculated by integration. Variations in calcite area per unit volume of solution have then been accounted for to allow direct comparison between the values of concentration and time obtained directly by experiment and the ones calculated by integration. Sets of the lowest experimental values of concentration of $Ca(HCO_3)_2$ and time corresponding to a reliable measurement of the surface concentration of Sc^{3+} have been chosen as starting points for the integration. The results of the integration are shown as curves on Figs. 2 and 4. It can be seen that eqn. (3) gives a good representation of the measurements except at the highest and lowest concentrations of Sc^{3+}. Unfortunately, it is at the moment not possible to give any quantitative statement as to what extent the discrepancies are caused by experimental errors or by approximations in the procedures of calculation.

Interpretation of the results. It is of interest to find a theoretical explanation for the empirical correlation represented by eqn. (3).

An introductory investigation of the mathematical properties of the correlation shows two limiting conditions which have to be accounted for by a satisfactory theory.

Firstly, this equation indirectly embodies the idea of an apparent equilibrium, the rate of reaction being very close to zero at a concentration of $Ca(HCO_3)_2$ given by eqn. (4):

$$C_{(r=0)} = C_{\text{real}}{}^* - (k'/k'')\ \overline{C}_{\text{Inh}} \tag{4}$$

The concentration of $Ca(HCO_3)_2$ giving zero reaction rate should thus be dependent upon the amount of inhibitor adsorbed.

Secondly, eqn. (3) shows that the rate of reaction at zero concentration of $Ca(HCO_3)_2$ depends upon the surface concentration of inhibitor as expressed by eqn. (5).

$$(\mathrm{d}C/\mathrm{d}t)_{(c=0)} = k'C_{\text{real}}{}^* - k''\ \overline{C}_{\text{Inh}} \tag{5}$$

According to eqn. (5) the initial rate of reaction for an experiment started with particles already contaminated with inhibitor is predicted to be lower than for an experiment with pure particles. Experiment No. 7 on Fig. 5 in agreement with this statement shows a tendency towards a reduced rate of reaction at lower concentrations of $Ca(HCO_3)_2$, the point at 0.8×10^{-3} M being discarded for reasons explained before.

At present, 3 different reaction mechanisms may be suggested to explain the inhibitory action:

1. Based upon the limited information then available, Terjesen *et al.*[2] tentatively suggested that the inhibiting cations were adsorbed together with an equivalent amount of CO_3^{2-} ions. This increase in the surface concentration of CO_3^{2-} ions caused by the inhibition was supposed to speed up the reverse reaction and thus reduce the overall rate of dissolution. These ideas lead to formulae of the type

$$\mathrm{d}C/\mathrm{d}t = k'\ (C_{\text{real}}{}^* - C) - f\ (\overline{C}_{\text{Inh}},\ C) \tag{6}$$

the function f having the properties

$$f(0,\ C) = 0$$
$$f(\overline{C}_{\mathrm{Inh}},\ 0) = 0$$

The rate of dissolution for zero concentration of Ca^{2+} ions is then independent of the surface concentration of inhibitor ions. This is contrary to the experimental evidence represented by the empirical eqn. (3). The theory also predicts, in contrast with later experimental evidence, that the inhibitor is desorbed if the concentration of $Ca(HCO_3)_2$ is increased above C_{app}.* It does, however, lead to the concept of an apparent equilibrium.

2. A second explanation may be provided by a theory based on the idea that the removal of Ca^{2+} and CO_3^{2-} ions from the calcite lattice cannot take place except by simultaneous hydration of the ions by the water molecules present in the adsorption layer. The adsorption layer also contains Ca^{2+} ions and inhibitor ions in hydrated form. When the concentration of these hydrated ions in the surface layer increases, the amount of adsorbed water which is free to react will decrease and finally become zero. According to this notion the rate of dissolution will be proportional to the concentration of free water molecules in the adsorption layer. If we designate the concentration of water molecules in the absence of any Ca^{2+} or inhibitor ions by $\overline{C}_0$, the concentration of adsorbed Ca^{2+} ions by $\overline{C}_{\mathrm{Ca^{2+}}}$ and the concentration of adsorbed inhibitor ions by $\overline{C}_{\mathrm{Inh}}$, the rate of dissolution becomes:

$$\frac{\mathrm{d}C}{dt} = k_1\ (\overline{C}_0 - k_2\overline{C}_{\mathrm{Ca^{2+}}} - k_3\overline{C}_{\mathrm{Inh}}) \quad (7)$$

k_1, k_2, and k_3 are constants.

By assuming a Freundlich type adsorption isotherm to apply, the surface concentration of Ca^{2+} ions can be replaced by the bulk concentration:

$$\overline{C}_{\mathrm{Ca^{2+}}} = k_4 C^{1/m} \quad (8)$$

$\overline{C}_0$ can be determined by the condition that the rate of dissolution is zero when $C = C_{\mathrm{real}}*$ and $\overline{C}_{\mathrm{Inh}} = 0$:

$$\overline{C}_0 = k_2 k_4 C_{\mathrm{real}}*^{1/m} \quad (9)$$

or

$$\frac{\mathrm{d}C}{dt} = k'(C_{\mathrm{real}}*^{1/m} - C^{1/m}) - k''\ \overline{C}_{\mathrm{Inh}} \quad (10)$$

By giving m the value of one, the empirical eqn. (3) is obtained.

According to this theory the rate of dissolution becomes zero when all the water molecules are engaged by the adsorbed cations. The experiments, however, show that there is a very small but observable rate of dissolution also beyond the apparent equilibrium.

The hydration theory is, not capable of explaining how a chemical compound can inhibit the dissolution as well as the growth of a crystal of a given material and in addition modify the shape of the growing crystal.[13,14] Neither can it explain the promoting effect of EDTA and CN^- upon the dissolution of CaF_2.[3]

3. The deficiencies of the hydration theory lead to a third theory assuming that the inhibiting ions are effective because they block the active spots or "kinks" in the crystal lattice where the removal of ions can take place. According to this theory, the rate of dissolution is assumed to be equal to the product of the number of kinks and the rate of movement of an individual kink.

Let $\overline{C}_0$ be the total surface concentration of kinks, $\overline{C}_{Ca^{2+}}$ the surface concentration of kinks blocked by an adsorbed hydrated Ca^{2+} ion, and $\overline{C}_{Inh}$ be the surface concentration of kinks blocked by an inhibitor ion. The rate of dissolution may then be expressed as

$$\frac{dC}{dt} = k'' \ (\overline{C}_0 - \overline{C}_{Ca^{2+}} - \overline{C}_{Inh}) \tag{11}$$

An experiment with no inhibitor present shows that

$$k'' \ (\overline{C}_0 - \overline{C}_{Ca^{2+}}) = k' \ (C_{real}{}^* - C) \tag{12}$$

which inserted into eqn. (11) gives the empirical equation (3).

Besides leading to a mathematical model describing the experimental results, the kink theory is also capable of explaining that an inhibitor to the dissolution of a compound may even be an inhibitor to its crystallization. The promoting effects of the complexing agents EDTA and CN^- upon the dissolution of CaF_2 [3] could according to this theory be explained as the result of an interference with the adsorption of Ca^{2+} ions. The low rate of dissolution observed at concentrations higher than the apparent equilibrium may be attributed to the formation of new kinks which are not readily blocked by inhibitor ions. This explanation also agrees very well with the works of Ives [10] mentioned previously.

The curves on Figs. 6, 7, and 8, showing that the amount of inhibitor adsorbed increases even after an equilibrium concentration of $Ca(HCO_3)_2$ has been reached, indicate that the kinks are not the only sites of adsorption. It is thus necessary to assume that the kinks will be occupied before adsorption on other sites takes place to any appreciable extent.

CONCLUSION

The kink theory seems to offer the simplest and most convincing explanation of the experimental results. It is furthermore in accordance with the results obtained during other studies of the effects of inhibitors. The kink theory is for this reason thought to represent the best physical model for the mechanism of inhibition among the 3 models suggested.

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