# The Calcium Binding Capacity of Polycarboxylates

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**It can be shown both theoretically and experimentally that calcium carbonate forms during the titration of polycarboxylates by calcium with carbonate as the indicator, and that the calcium carbonate is dispersed by the polycarboxylate. If the dispersing capacity of the polymer exceeds the level of calcium carbonate present, the precipitation of the calcium salt of the polymer is observed as the end point. If the quantity of carbonate is increased to a level greater than that of the dispersing capacity of the polymer, the precipitation of calcium carbonate is observed as the end point, and we term the result of this titration the "calcium carbonate dispersing capacity."**

The precipitation of sparingly soluble alkaline earth and heavy metal salts causes problems in virtually all processes in which untreated water is heated. Areas affected include industrial and domestic cleaning, power generation, and a variety of production processes. The consequences are, to name a few, the formation of scale on heat exchangers, blocked pipes, valves, and nozzles, and the incrustation of laundry.

Methods to counteract these phenomena are based on one of two principles. One is to inhibit the growth, but not the formation, of sparingly soluble crystals and, at the same time, to disperse the nuclei that have already been formed. The dispersion obtained in this manner cannot settle or form scale. This method is mainly used in closed cooling circuits or in large-scale industrial evaporation processes, such as the desalination of seawater or sugar refining. The amount of substance required to inhibit crystal growth is in the region of a few ppm.

The second principle is to prevent the initial formation of sparingly soluble salts, as in washing and cleaning processes. Here, the complexing and dispersing capacity of a substance is more important than its ability to inhibit crystal growth. Much larger quantities are required, and substances that have a purely complexing function need to be added in stoichiometric proportions.

Complexing agents, such as aminopolycarboxylic acids, provide the simplest means of preventing the formation of sparingly soluble salts, especially alkaline earth salts. The only prerequisite is that their complex formation constants with the metal ions in question are sufficiently high. The method devised by Schwarzenbach (1) is the most accurate one available for the determination of complex formation constants. However, the method itself and the subsequent calculation is rather complicated. A great deal of effort has been put into experiments to find different ways of calculating these and other similar constants. The term "calcium binding capacity" has often played a part in these efforts.

This paper is concerned with the definition of the properties of complexing agents and dispersants described by the term "calcium binding capacity". Complexing agents form chelates with a certain quantity of metal ions—this quantity can be referred to as the "complexing capacity". On the other hand, the complex formation constant indicates the strength of a complex. Because of the methods

used to determine them, "binding capacity" can be equated with "complexing capacity", but the former is often erroneously held to correspond to the strength of the complex. Information on the effectiveness of a complexing agent can only be provided by the complexing capacity and the complex formation constants in conjunction, they have little significance on their own. This is especially true of the complexing capacity, which is nearly always quoted, as it is held to have practical significance. Products with a low complexing constant can have a high complexing capacity, depending on how the experiment is set up, and yet still be completely ineffective.

Since the arrival of calcium-selective electrodes, it has been possible to determine the complex formation constant and the complexing capacity at the same time. Various mathematical methods have been suggested for calculating these values (2-8). In some cases, factors may be derived that serve as a measure for these two figures (9). Complex formation constants determined in this way depend on the nature and concentration of other dissolved substances, particularly those of an ionic nature. Another point to consider is that the constants of polymeric complexing agents are influenced by other factors, such as the degree to which the active sites on the polymer are occupied by calcium ions (10). This explains why calcium complex formation constants between $10^2$ (3) and $2 \times 10^5$ (6) are described for polyacrylic acids. Our experiments at pH 9.5 and an ionic strength of 0.08 M KCl have given values of about $3 \times 10^4$.

These methods are united by the fact that they only describe the interaction between the sequestrant and the metal ions in isolation. As we shall see, the interaction between the sequestrant and the alkaline earth salt—the formation of which needs to be prevented—is of great importance in describing the effectiveness of a sequestrant.

It would be appropriate at this point to briefly review the methods of titration, as compared to calcium in the presence of an indicator, that are used to determine the "calcium binding capacity" or "calcium complexing capacity" of complexing agents.

Anions that form sparingly soluble salts with calcium are generally employed as indicators. These anions include oxalate (11,12) and carbonate (13,14), capronate (15) and iodate (11) are encountered less frequently. The best known method is the Hampshire Test (13,14) which is generally recognized in the detergents industry as a test for incrustation inhibitors in laundry detergents. For this test, a 1-2 g sample is dissolved in 100 ml of distilled water. Caustic soda is added to acidic solutions until they are neutral. 10 ml of a 2% sodium carbonate solution is then added. The solution is then titrated against a 0.25 m calcium acetate solution at pH 11 until lasting turbidity is observed.

Turbidity titration methods such as these primarily indicate the quantity of calcium ions complexed per unit of complexing agent. Results are usually expressed as the quantity of bound calcium carbonate. Spurious results can be obtained if the complexing agent's formation con-

stant with calcium (which is normally unknown) is too small to prevent the formation of the sparingly soluble indicator salt. On the other hand, an indicator can be selected that allows the order of magnitude of the complex formation constant to be determined. Because the end point of the titration depends on the quantity of indicator present, an approximate value for the complex formation constant can be determined (11). Because of the simplicity of the apparatus required this method is still in use today (16).

Reversing the process provides similar results. The substance to be tested is added to freshly precipitated calcium carbonate (2,17,18), oxalate (2), or oleate (2,3,10) until the latter is fully dissolved. Even heated, titration is inappropriate as the solution dissolves at a protracted rate. Also, the fact that the titrant has to be changed with each sample is an obstacle to the automation of this method.

The values obtained by this method nearly always correspond to those obtained by turbidity titration, but polymers have a considerable lower calcium binding capacity. One possible explanation is that precipitation is delayed, possibly owing to the presence of impurities (17).

There are other methods of determining sequestering capacity. For instance, insoluble sequestrants (such as ion exchangers) are tested by adding them to hard water and then measuring the residual hardness after a certain time has elapsed (19,20). Less common methods include the use of soapy hard water as an indicator (21), in which the formation of foam indicates the end point; the measurements of the retention of calcium ions in solutions that are treated with swatches impregnated with soap (22); and the photometric measurement of calcium carbonate deposits on microscopic slides (23).

*Turbidity titration.* The Hampshire nephelometric titration is used mainly because of its simplicity. This method was developed specifically for complexing agents, and gives reliable results for substances that produce strong complexes. With substances that produce weaker complexes (e.g., nitrilotriacetic acid (NTA)) the situation is different.

If the strength of the bond between the calcium ion and the complexing agent approaches that of the bond between the calcium and carbonate ions, the end point of the titration will give a result that is below the stoichiometric equivalence point.

We introduced a few simplifications into the Hampshire method and used a computer to generate a set of curves for the titration of NTA. We used the stability constant for an ionic strength of 0.1 (pK=6.4), and we assumed that the activity coefficients of the ions were constant.

We used the following equation, which is obtained by solving the law of mass action for the quantity of bound calcium using the known quantities of total calcium and total complexing agent present.

$$K = [MeCA] / [Me_f] [CA_f]$$

with $[MeCA] = [Me_b]$; $[Me_f] = [Me_{tot} - Me_b]$;

$$[CA_f] = [CA_{tot}] - [Me_b]$$

results in

$$[Me_b] = Z - \sqrt{Z^2 - [Me_{tot}] [CA_{tot}]}$$

where

$$Z = (1 + K([Me_{tot}] + [CA_{tot}])) / 2 K$$

$$[Me_f] = [Me_{tot}] - [Me_b]$$

| Me | = metal ion |
|---|---|
| CA | = chelating agent |
| index "f" | = free |
| index "b" | = bound |
| index "tot" | = total |
| K | = stability constant |

As soon as the concentrations of free calcium and carbonate exceed the solubility product of calcium carbonate, the calcium carbonate precipitates. We have allowed
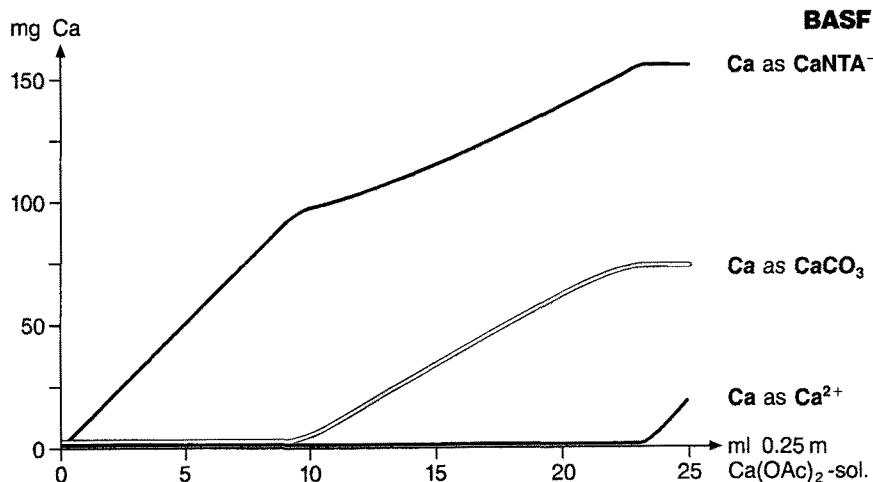


FIG. 1. Calculation of the titration of Na₃NTA according to Hampshire method.

for this in our calculations. Curves such as those shown in Figure 1 are obtained. As soon as calcium carbonate begins to form the curve for calcium–NTA is inflected. When the carbonate ions and complexing agents have been consumed, the concentration of free calcium ions finally begins to increase. The real equivalence point is approximately one-third higher than the point at which calcium carbonate forms. However, because the observed turbidity appears later than the curve would suggest, the results are fairly accurate.

If we perform the same calculation for a complexing agent that forms even less stable complexes (e.g., a polycarboxylate with a stability constant of $3 \times 10^4$), the situation becomes completely different (Fig. 2). It is clear from the calculation that calcium carbonate will form initially, but we do not observe any turbidity.

The reason is that polycarboxylates have a dispersing effect. This very important property of polycarboxylates can be measured only by this type of titration, it cannot be measured by calcium-selective electrodes. This fact leads us to the main point of this paper. All the calcium carbonate formed during the Hampshire titration—that is to say, a maximum of 190 mg calcium carbonate—will be completely dispersed by any polycarboxylate with medium-to-high dispersing power. Nevertheless, the end point of the titration is still observed. But the precipitate is not calcium carbonate, it is calcium polycarboxylate. This end point is an indication of the solubility of the calcium salt of the polymer, and not of its binding capacity for calcium. The solubility of calcium polymers is an interesting subject in its own right, but it does not correlate with the dispersing capacity of polycarboxylates. It is
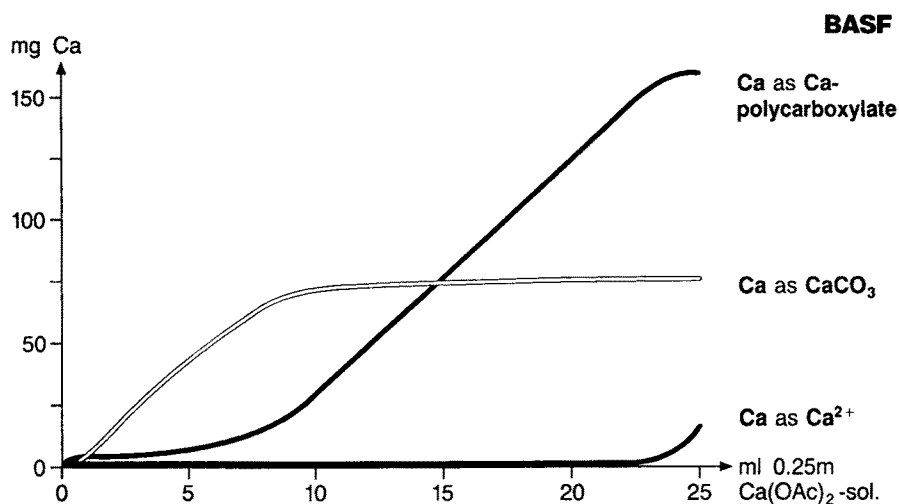


FIG. 2. Calculation of the tiltration of polycarboxylate according to Hampshire method.
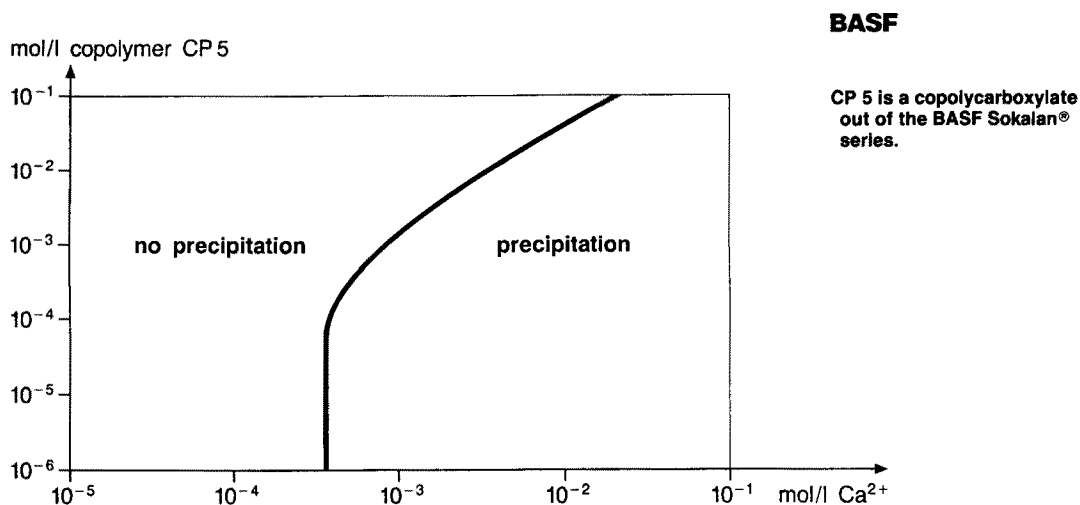


FIG. 3. Precipitation of copolymer CP 5 Bioelimination.

the dispersing capacity of polycarboxylates that is important in inhibiting the incrustation of fabrics.

As can be seen in Figure 3, the fact that polycarboxylates form sparingly soluble salts is very convenient. This curve shows the solubility of a carboxylic copolymer, CP 5, as a function of the concentration of calcium ions and copolymer. There is a definite point at which up to 90% or more of the polymer will immediately precipitate. The left-hand side of the curve applies to the conditions found in the washing machine, whereas the right-hand side of the curve applies to the waste water, where the polymer concentration is low. The calcium salt of the polymer thus precipitated is then eliminated from the waste water by adsorption onto the activated sludge.

The individual processes at work in the turbidity titration can be illustrated by titration in the presence of different amounts of carbonate. A polyacrylic acid with a relative molar mass of 250,000 provides a pertinent example. The titration is performed according to a slightly modified Hampshire method. 1 g of polymer is dissolved in 100 ml of water and neutralized. 200, 300, and 500 mg of sodium carbonate are added. The pH is adjusted to 11 and is maintained constant during the titration. The titrant is a 0.25 M calcium acetate solution. In the next curve (Fig. 4), we have plotted the transmission of the solution against the amount of calcium acetate added. In the presence of 200 mg sodium carbonate (this corresponds to the Hampshire test), the polymer disperses all the calcium carbonate that forms. The turbidity at the end of the titration is due to the precipitation of calcium polyacrylate. The presence of 300 mg sodium carbonate slightly exceeds the dispersing capacity of the polymer. The excess calcium carbonate is visible in the form of a slight turbidity which hardly increases during the course of the titration until the end point is reached. The presence of 500 mg sodium carbonate is well in excess of the dispersing capacity. In this case, the end point of the titration occurs when calcium carbonate
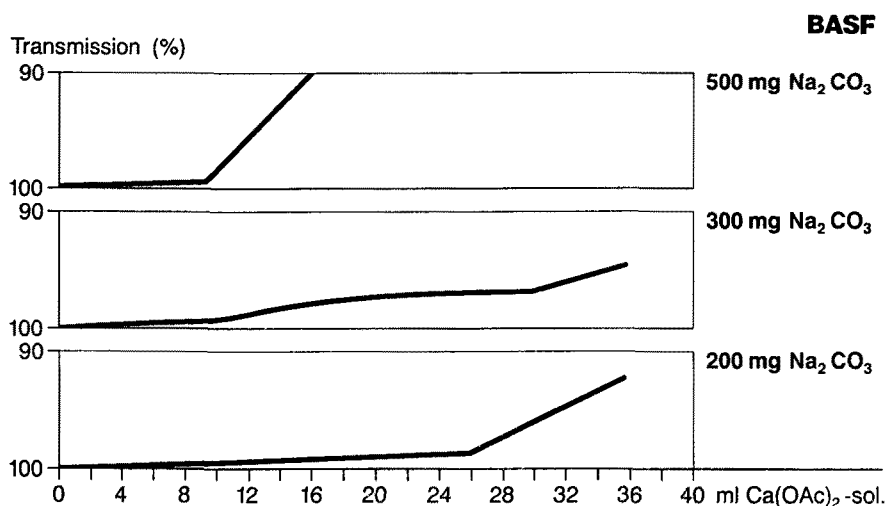


FIG. 4. Tiltration of polycarboxylate in presence of different amounts of carbonate.
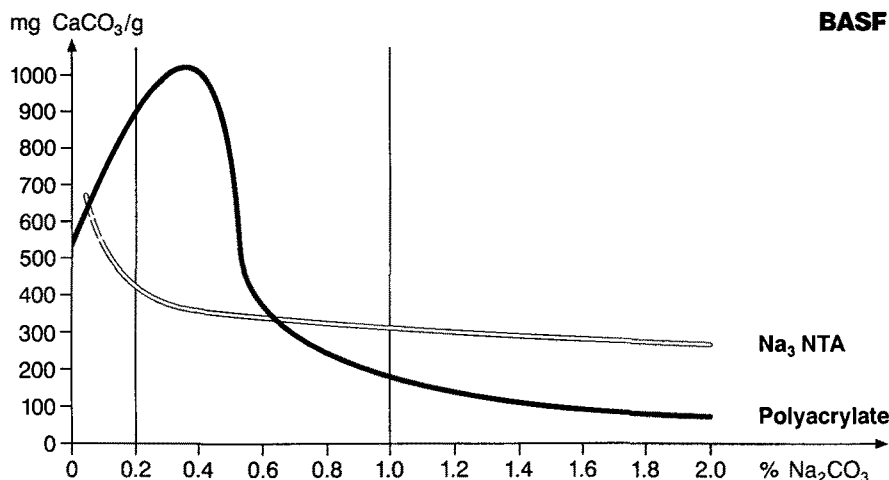


FIG. 5. Results of the turbidity tiltration as a function of carbonate concentration.

begins to form, and we call the value obtained at this point the calcium carbonate dispersing capacity (CCDC).

If we plot the end point against the quantity of sodium carbonate present (Fig. 5) we see that with NTA no turbidity occurs in the absence of carbonate. As the carbonate content increases, less calcium acetate is required for precipitation, this is to be expected owing to the competition between carbonate and NTA for calcium.

With polycarboxylates we obtain a very interesting curve. We used the same polyacrylate here as in the previous example. In the carbonate-free solution, the end point is reached when calcium polyacrylate precipitates. The end point is delayed by the presence of small quantities of carbonate, as some calcium ions will be bound as calcium carbonate, which will not precipitate because of the dispersing effect of the polyacrylate. This illustrates the synergism that occurs between the carbonate and the polymer. If either were present alone, the calcium carbonate or calcium polyacrylate would precipitate. The presence of both ot them inhibits precipitation, but this is only valid for small concentrations of carbonate. Finally, at high concentrations of carbonate ions calcium carbonate precipitates and the end point of the titration gives a true figure for the calcium carbonate dispersing capacity.

Therefore, it follows that turbidity titrations should be performed with concentrations of carbonate that correspond to the calcium carbonate dispersing capacity. This is especially important for products that have a dispersing effect, but also for products whose mode of action is unknown or has not been conclusively defined, such as phosphonates. Therefore, we suggest the test method for dispersing agents listed in the Experimental section.

## EXPERIMENTAL

*Reagents.* Sodium carbonate ($Na_2CO_3$), hydrochloric acid, and caustic soda (NaOH), all 99.5% pure, were supplied by Merck. Only deionized water was used in these experiments. A 0.25 M calcium acetate solution prepared from pure calcium acetate ($Ca(OAc)_2$) which was supplied by Janssen Chimica, Belgium, was used for the titration.

*Equipment.* Titroprocessor (Metrohm 672) with two Multi-Dosimats (Metrohm 655) was employed for calcium acetate and caustic soda. The pH was monitored and maintained at a constant level with a pH meter (Metrohm 652) fitted with a Na-glass electrode (Schott N 65), and an Impulsomat (Metrohm 614). The temperature was held constant during titration with a Haake N3 thermostat. The increase of turbidity was monitored with a photometer (Metrohm 662), fitted with fiber optics, at a wavelength of 650 nm.

*Procedure.* Dissolve 1.0 g of the dispersing agent in 100 ml deionized water. If necessary, neutralize with 1 M caustic soda solution to prevent loss of carbonate. Then add 10 ml 10% (wt/wt) sodium carbonate solution. Adjust pH with caustic soda or hydrochloric acid as required. During titration, pH and temperature are maintained constant. The increase in turbidity is automatically monitored.

Figure 6 shows the results with several different polymers with various amounts of sodium carbonate as in the previous example. If we compare the results obtained with 0.2% sodium carbonate—the concentration in the original Hampshire method— with the results with 1% sodium carbonate—the concentration with which we work—the order in which the products appear would be reversed in some cases. Polyacrylates, for instance, often give considerably higher results at 0.2% sodium carbonate than copolymers because of the higher solubility of the Ca-polymer salts. On the other hand, copolymers have a higher true dispersing capacity for calcium carbonate than homopolymers, as the results at 1% sodium carbonate show. These observations have been validated by washing tests.

The results of our turbidity titration naturally depend on the pH of the solution, because both the stability constant of the polymer and the equilibrium between carbonate and hydrogen carbonate vary with pH.

With the equilibrium constant of $4.8 \times 10^{-11}$ it can be calculated that the ratio of $CO_3^-$ to $HCO_3^-$ is 4.8 at pH 11, but only 0.48 at pH 10, and so on. Therefore, the apparent concentration of $CO_3^{2-}$ at lower pH values is too low for $CaCO_3$ to precipitate, and we observe high values for the



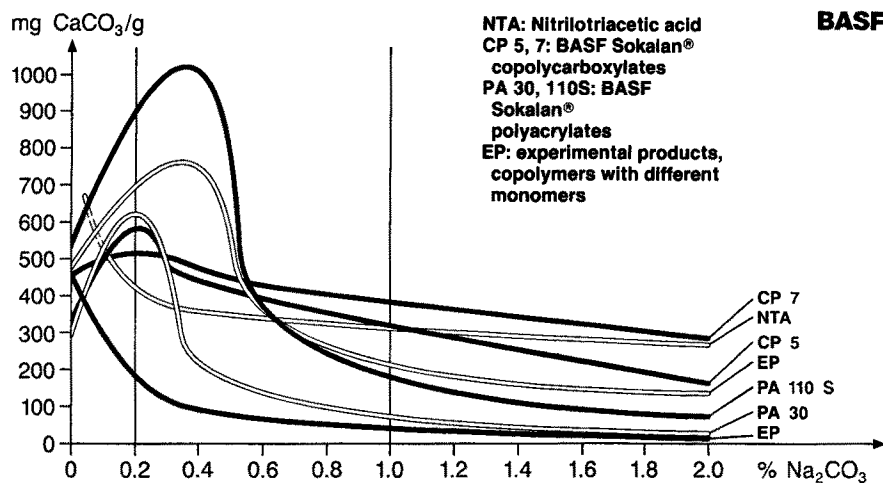FIG. 6. Result of the turbidity titration as a function of carbonate concentration.
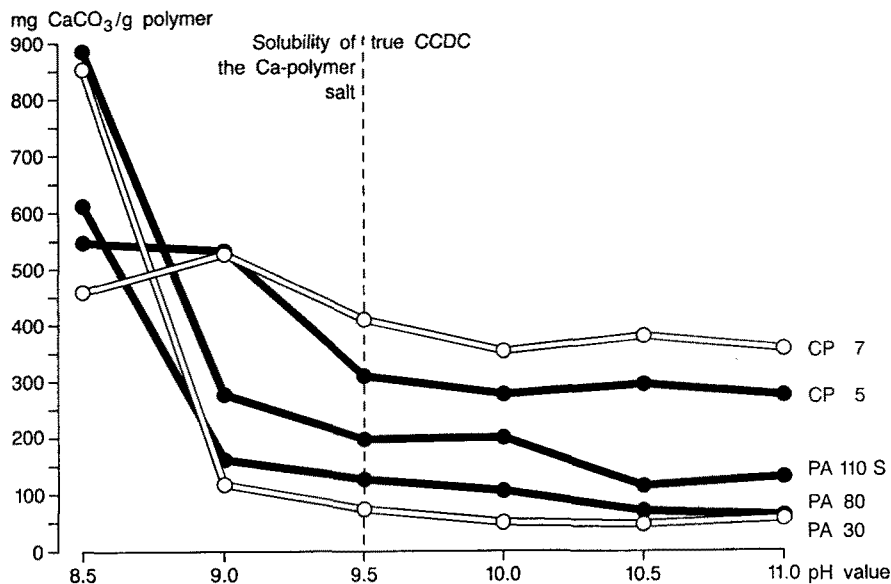
**FIG. 7. CCDC versus the pH value.**

CCDC (Fig. 7). This indicates that the calcium salt of the polymer is the precipitant.

To go into more detail, a CCDC of 250 mg $CaCO_3$ for polymer CP5 means that there has to be more than 250 mg $CaCO_3$ in the test solution for an insoluble excess of $CaCO_3$ to form at the end point of the titration. If no $Ca^{2+}$ ions are present, the available concentration of $CO_3^{2-}$ can be calculated from the law of mass action with $K_s$ as the equilibrium constant:

$$[CO_{3\ free}^{2-}] = K_s \ [CO_{3\ total}^{2-}] \ / \ [H^+] + K_s$$

with $[CO_{3\ total}^{2-}] = [CO_{3\ free}^{2-}] + [HCO_3^-]$.

$CaCO_3$ precipitates as soon as $Ca^{2+}$ is present, but we are still a long way from the equivalence point. Therefore, we can assume that the molar amount of precipitated $CaCO_3$ is approximately equal to the molar amount of $Ca^{2+}$ that was added. The amount of total $CO_3^{2+}$ has to be reduced by this value, and we can thus derive the following equation from the previous one.

$$[CO_{3\ free}^{2-}] = K_s \ ([CO_{3\ total}^{2-}] - [Ca^{2+}_{\ total}]) \ / \ [H^+] + K_s.$$

A polymer like CP5, which has a CCDC of about 250 mg $CaCO_3/g$, disperses all the calcium carbonate present until this figure is reached and then precipitation begins to occur. The concentration of total calcium at this point is 100 mg/g polymer. Given the total amount of carbonate present in the test (1000 mg of sodium carbonate=566 mg $CO_3^{2-}$, we can use the above equation to calculate the amount of available $CO_3^{2-}(=[CO_{3\ free}^{2-}])$ present at the onset of precipitation of $CaCO_3$.



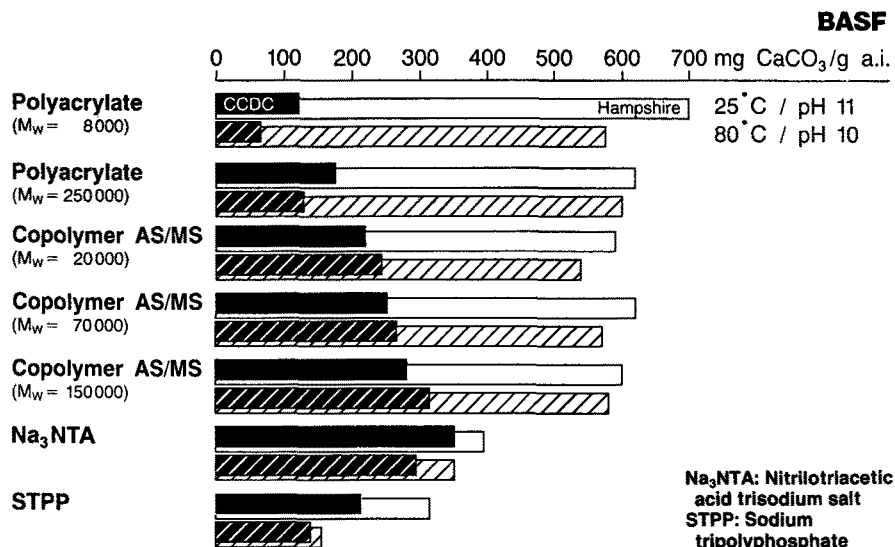**FIG. 8. Results of the turbidity titration in the presence of 1.0 g $Na_2CO_3$ (CCDC) and 0.2 g $Na_2CO_3$ (Hampshire).**

| pH | 11 | 10 | 9.5 | 9.0 |
|---|---|---|---|---|
| % $[CO_3^{2-}{}_{free}]$* | 60 | 24 | 9.7 | 3.3 |

*Expressed as a percentage of $[CO_3^{2-}{}_{total}]$.

The above table clearly shows that at a pH of less than 9.5 the excess of free $CO_3^{2-}$is too low for $CaCO_3$ to precipitate in the presence of polymers like CP5. The previous equation also shows that the amount of available $CO_3^{2-}{}_{free}$ increases if the CCDC is lower, i.e., if the value for $Ca^{2+}{}_{total}$ is lower at the point of precipitation. This means that $CaCO_3$ still precipitates at lower pH values.

We were able to verify this in an experiment (Fig. 7). In following the curve, it becomes evident that the point where a constant CCDC is reached—i.e., the point where $CaCO_3$ precipitates—is shifted to higher pH values with an increase in CCDC. Therefore, true values can be measured if the pH is greater than 9.5 (with the given total amount of carbonate used in this test). This pH range is also the working area for laundry detergents. We chose the highest possible value (pH 11) for the titration at room temperature, and a lower value (pH 10) for the titration at elevated temperatures (80°C) in order not to damage the electrode.

Finally, Figure 8 compares the results of the turbidity titration in the presence of 0.2% sodium carbonate according to the Hampshire Test, and 1% sodium carbonate as described in our method for the determination of the calcium carbonate dispersing capacity. The results obtained with our method, as could be expected from Figure 6, are generally lower than those obtained in the Hampshire Test. The polymers also appear in a different order of rank. However, it is the CCDC that corresponds with the anti-incrustation efficiency of the polymer as determined in washing tests.

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