INFLUENCE OF PH ON THE FORMATION OF POLYPHOSPHATE COACERVATES.

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Abstract The coacervation of polyphosphates usually takes place at very low pH value. We show that, in the system $\text{Na}_2\text{O}-\text{CaO} - \text{P}_2\text{O}_5$, the decrease of pH is due the hydrolysis of the terminal P-OH groups and that it is a consequence of the coacervation. So a very low pH is not necessary to obtain a coacervate and it is possible to form coacervates in non-acid media (even basic). The same results are obtained with other precursor systems of polyphosphate coacervates. These results may be interesting for the achievement of coacervates as industrial glasses precursors.

INTRODUCTION

Polyphosphate glasses have some potential industrial uses because of their own properties which often differ from those of silicate glasses, particularly their thermal characteristics¹. An interesting way for their elaboration comes from a colloidal route : the coacervates of polyphosphate²⁻⁴. Coacervation is a liquid-liquid phase separation that permits to segregate a colloid rich phase. The first originally works are 68 years old, they concern organic compounds⁵. Coacervates of polyphosphate have rather recently been reported by Kanazawa and all^{2, 6}.

Polyphosphate coacervates present some interests for industrial applications because of their rheological behaviour that allows their use for processes like enamelling, glazing and as binder aid for ceramics sintering^{4,7-9} before curing. Nevertheless we have to control the chemical and physical properties of coacervates as their conditions of preparation^{6,10}.

An important parameter of this process which have to be controlled is the pH during coacervation. Two consequences of the pH control may be notified. First this permits to adapt the reactivity of coacervates with the metal or the ceramic used in coating or glazing processes for example. In a second way, it is possible to increase the lifetime of coacervates by modifying pH value : hydrolysis of polyphosphate chains increases at once with temperature and the weak values of the pH of supernatant solution¹¹.

In fact, previous old works of our laboratory have indicated that coacervates are only obtained in very acidic media, and that gel phases appear in basic media^{12, 13}. This theory has been always more recently proposed by another team for the achievement of zinc-polyphosphate coacervates¹⁴. A simple experiment would confirm this theory. Coacervates are essentially constituted by long chains of polyphosphates, around 25 phosphate groups in average. By ^{31}P NMR study (see figure 1) of calcium-sodium coacervates (which are obtained by action of calcium chloride on sodium polyphosphates in acidic media), we only obtain two peaks. The first one, at 17-20 ppm, with orthophosphoric acid as reference ppm = 0, corresponds to the median O-P-O groups, and the second one at 7-12 ppm is due to the terminal groups. Their ratio permits us to evaluate the average chain's length of polyphosphate compounds. For a gel, obtained by addition of calcium oxide on sodium polyphosphate in aqueous solution¹² (so in basic media), we obtain a more complex ^{31}P NMR spectra (figure 1) with the apparition of numerous phosphate species. If we start from the previous coacervate, an addition of soda increases the pH and the compound turns into a gel a few days later. The time dependence of ^{31}P NMR analysis is shown on figure 2. Hydrolysis of polyphosphates induces the formation of short chains such as pyro and

FIGURE 1 ^{31}P NMR of calcium-sodium coacervate and gel.

FIGURE 2 Evolution of a sodium-calcium coacervate with NaOH followed by ^{31}P NMR spectroscopy.

orthophosphates. This may explain the formation of a gel. But the rate of hydrolysis of coacervates in basic media is low and this does not prove the impossibility of obtaining the coacervation in a non acidic medium.

EXPERIMENTAL DATA

Influence of the pH on coacervation in the system $\text{CaO} - \text{Na}_2\text{O} - \text{P}_2\text{O}_5$.

By mixing calcium chloride and sodium polyphosphate solutions, a coacervate is obtained. This one has an acid pH. For example, if we start from a solution of $(\text{NaPO}_3)_n$ (3M) with a pH 4.7, and a CaCl_2 solution (2M) with a pH 4.2, we obtain a coacervate with a supernatant solution at a pH 2.7. This result is not coherent with a simple mix of the two solutions. Polyphosphoric acid is a strong acid and only the terminal P-OH groups of chains have a weak acidity¹⁵. The increase of acidity may be only attributed to a release of protons from these terminal chains, because at this pH value, calcium ions do not give a completion phenomenon with hydroxyl of the aqueous solution. This hypothesis is corroborated by the fact that in a previous study¹⁶, we have shown a lack of calcium hydroxide in both coacervate and supernatant phases.

To explain this decrease of acidity, we use the theory developed in a previous work¹⁷. The additions of Ca^{++} ions to the solution of Graham's salt (sodium polyphosphate) permits to hide the negative electrostatic charges of polyphosphate chains. This phenomenon contributes to the destabilisation of the aqueous system (if less electrostatic repulsion between polyphosphate chains are present, these chains may come together to form the coacervate and the destabilisation occurs). To avoid this destabilisation, polyphosphates have to release protons from their terminal P-OH groups. Then, the charge density of the colloid does not decrease and the system remains stable in this step. Then, for a larger quantity of free protons, an equilibrium is attempted and another addition of calcium salt permits the direct formation of coacervate by agglomeration of polyphosphate chains.

Control of the pH during coacervation.

From the last remark, it should be possible to obtain coacervates in no highly acid conditions. To check this possibility we have made several experiments. In each case we have started from two solutions. The first is a $(\text{NaPO}_3)_n$ (3M) and the second is a CaCl_2 solution (2M). The pH of these solutions have been adjusted using chlorhydric acid or sodium hydroxide. Coacervation has been obtained by a mix of one volume of calcium solution with two volumes of polyphosphate solution. To avoid the formation of calcium hydroxide, we have always worked at a pH lower than 12.

Using this way, it has been possible to obtain coacervation at pH values higher than 2.7. Figure 3 shows our results. pH of the initial sodium polyphosphate solutions used are represented on abscissa and pH of the initial calcium chloride solutions used appear in ordinate. 30 minutes

after formation of the coacervate, the pH of the supernatant liquid is measured. All the points on figure 3 show the coacervate formation. The dotted lines pointed out correspond to isopH lines. They are essentially controlled by the pH of the initial polyphosphate solution. For each case we have noticed a falling value of the pH of supernatant liquid of about 2 units beside the pH value of the polyphosphate solution.

FIGURE 3 Influence of the initial pH of calcium chloride and sodium polyphosphate solutions on coacervation at 25 °C. The value of the supernatant liquid pH appears on the diagram.

The pH evolution of calcium chloride solution only produces a weak effect. Nevertheless, for acid medium of polyphosphate solution, we obtain not viscous coacervate (around 7000 mPa.s) which are in white points in the diagram of figure 3. On the contrary, viscosity increases (up to 45000 mPa.s) in basic media.

DISCUSSION

These results show the possibility of obtaining polyphosphate coacervates in both acid and basic media, whereas starting from calcium oxide one obtains a gel. To explain this phenomenon we have studied the influence of the counter-ion for calcium salts on coacervate formation. These counter-ions may induce the formation of complexes with cations, and so this may decrease the charge density. A steric influence have also to be considered.

To give an answer for the influence of the counter- ions, we have studied at 25°C, the conditions of coacervate achievement using several counter-ions. By a usual graphical representation , we have plotted into a ternary diagram the critical condition of coacervation⁷ (figure 4). A line separates the diagram into two areas. The first one on the left side (figure 4) for the low percentages of electrolyte corresponds to the compositions for which a stable solution exists. The second - on the right side - corresponds to a two phases system : coacervate and supernatant liquid in equilibrium.

FIGURE 4 Equilibrium diagram of the liquid system {water – sodium polyphosphate – electrolyte}, in molar percents, obtained at 25 °C for several calcium salts.

The three counter-ions studied are chloride, nitrate, and formate. Figure 4 shows that the nature of the salt has not a strong influence on coacervation. Nevertheless, if no difference is noticed between nitrate and chloride salts, coacervation is only observed for dilute solutions in the case of formate.

The use of large anions like gluconate conducts to the formation of a gel¹⁹. The size of these anions may induce a disturbance in the electrostatic interactions between anions and cations¹⁷. So to explain the formation of gel taking over from coacervate, we have made the following experiment. We have started from a mix of CaCl_2 and $(\text{NaPO}_3)_n$ at the limit of coacervation, in an acid medium. An amount of calcium hydroxide leads to the formation of a gel,

without a great increase of the pH. But a second experiment is more conclusive. To the same solution, at the limit of coacervation, an amount of fluorhydric acid brings out in some minutes to the formation of a gel. In this case the pH is always very acid. These experiments confirm the minor influence of pH on coacervates or gels formation. Another consequence of these results is the importance of the counter-ions in the coacervation process. For example, by capillary electrophoresis, we have showed⁷ that chloride ions are present into the coacervates and even their concentration may reached 5-6 mg per gram.

Extension to other coacervates of polyphosphate.

To confirm the results presented above, we have studied the influence of pH on other systems. In each case, we have started from an electrolyte solution at a constant pH which has been mixed to a sodium polyphosphate solution with variable pH. Figures 5, 6 and 7 show our results for sodium, manganese and magnesium coacervates. For each experiment, we have recorded the value of pH during the mixing, and we have reported this value at the beginning of coacervation. 30 minutes later, the pH of supernatant liquid has also been measured. Figures 5 and 6 show the results obtained for sodium and manganese. We notice that for these compounds, the medium can be basic when coacervation is achieved. Using magnesium, the final medium is always acid. This may be explained by the solubility product of magnesium hydroxide. Moreover, an addition of magnesium oxide conducts to a the formation of a gel.

FIGURE 5 Final pH values for coacervation and for the supernatant liquid versus the initial pH of the solution of sodium polyphosphate used. These results have been obtained using Sodium chloride as electrolyte.

FIGURE 6 Final pH values for coacervation and for the supernatant liquid versus the initial pH of the solution of sodium polyphosphate used. These results have been obtained using Manganese chloride as electrolyte.

FIGURE 7 Final pH values for coacervation and for the supernatant liquid versus the initial pH of the solution of sodium polyphosphate used. These results have been obtained using Magnesium chloride as electrolyte.

Finally, we have studied the formation of coacervates using zinc salts²⁰. Starting from zinc chloride, we obtain the coacervation phenomenon until pH 5; and starting from zinc nitrate until pH 4.5. These results are also discordant against these of reference 14.

CONCLUSION

We have showed that coacervation of polyphosphate solutions do not needs an acid pH. Results of coacervation for calcium-sodium cations and others systems have been presented. These results present some interests for the control of coacervation and of course for their stability along time. For industrial applications these results may be useful for the preparation of coacervates as precursors for polyphosphates glasses.

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