

## **THERMOBAROMETRIC ANALYSIS OF PHYSICO-CHEMICAL TRANSFORMATIONS OF COACERVATES AND GELS OF POLYPHOSPHATES**

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By thermobarometric analysis, we have investigated gels and coacervates of polyphosphates systems ( $x$  MO- $y$  P<sub>2</sub>O<sub>5</sub> - $z$  CaO- $n$  H<sub>2</sub>O, where  $M = \text{Na or Mg}$ ) and studied their physico-chemical transformations until 1000 bars. In every case, the same general shape is obtained for the thermobarograms. A strong pressure increment is first observed bounded to the expansion of the sample under temperature effect. Then, between 100 and 110°C, a free water release is detected by an important and progressive decrement of pressure issue from a strong volume decrement. At higher temperature, the hydrolysis of the systems is turned into pressure increments. Such experiments are the first showing that, by thermobarometric analysis, physico-chemical transformations can be easily studied. Moreover, for the first time, a negative volume change at a transformation obtained by increasing the temperature has been able to be observed by thermobarometric analysis.

### **Introduction**

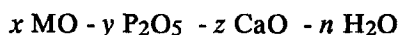
Gels and coacervates of polyphosphates show an increasing interest in coverings used in protection against oxidation [1]. Such systems are colloidal states obtained from solutions of polyphosphate macromolecules [2]. In coacervates, polyphosphates chains are tightly coiled, keeping "free water" included [3]. In gels, the presumed structure fit to micro-domains chains packing including the "free water" [3]. In both systems, "bonded water" exists. By increasing the temperature of these systems, very complex physico-chemical processes, such as free water release, hydrolysis, thermal condensation, appear [3]. Although the thermal behaviour under atmospheric pressure of such

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systems begins now to be understood [2–4], at our studies. Following our investigations by thermobarometric analysis of the behaviour under pressure of the phases transitions (first and second order or glass transitions) of organic compounds (monomers or polymers) [5–10], we have investigated the behaviour under pressure of the chemical transformations for solutions of mineral polymers, i. e. gel of calcium-sodium polyphosphates and coacervates of both calcium-sodium and calcium-magnesium polyphosphates.

### *Materials and method*

The studied compounds are:



where M = Na or Mg; such systems can exist, under atmospheric pressure, in both *gels* or *coacervates* states, according to the experimental way of elaboration [2]. Details on the preparation of these materials have been given elsewhere [2].

For both Ca-Na and Ca-Mg coacervates, the aim was to extend under pressure, the known results previously obtained by differential scanning calorimetry [3]. For gels, we have only investigated the Ca-Na system to compare its pressure behaviour to the coacervates's one.

Pressure studies were carried out in a Numerical Scanning Metabolemeter (M. A. B. 02 A-20, M. T. M. LEADER). The measurements consist by recording, versus the temperature, the pressure of a sample enclosed in a weakly dilatible cell [5, 8]. The samples are initially in fluid phase and fill the whole cell (20 cubic millimeters). Then, the experiments are performed at constant mass, and, for the temperature (+30, +180°) and pressure (0, +1 kbar) ranges, at quasi-constant volume [8]. The thermobarograms are plotted, for the three studied systems, at 2 deg/min heating rates.

### **Results and discussion**

Examples of thermobarograms obtained for coacervates of both calcium-sodium and calcium-magnesium and gel of calcium-sodium are reported in Figs 1 to 3 respectively. For each of the three systems, numerous samples have been studied, and the results are perfectly reproducible.

The general features of the thermobarograms for both Ca-Na and Ca-Mg coacervates (Figs 1 and 2) are similar. They always exhibit:

- an important pressure increment (part A-B),

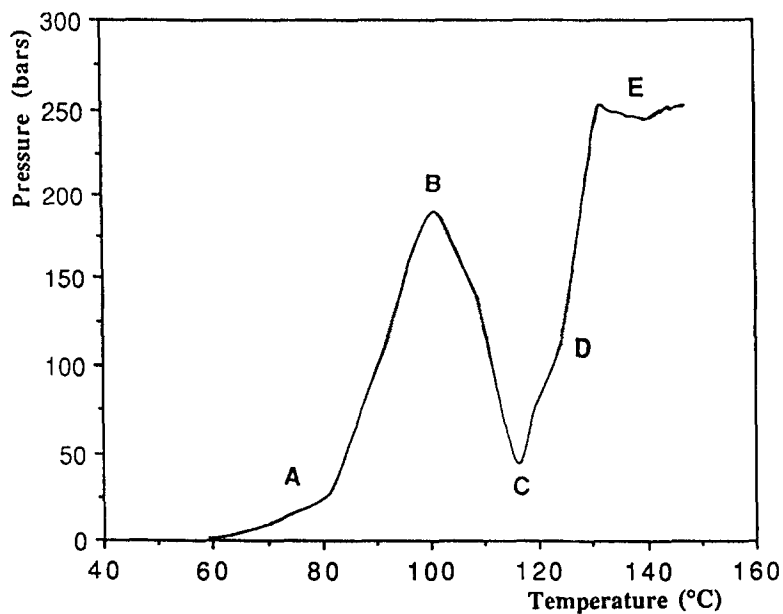


Fig. 1 Thermobarogram of Ca-Na polyphosphate coacervate

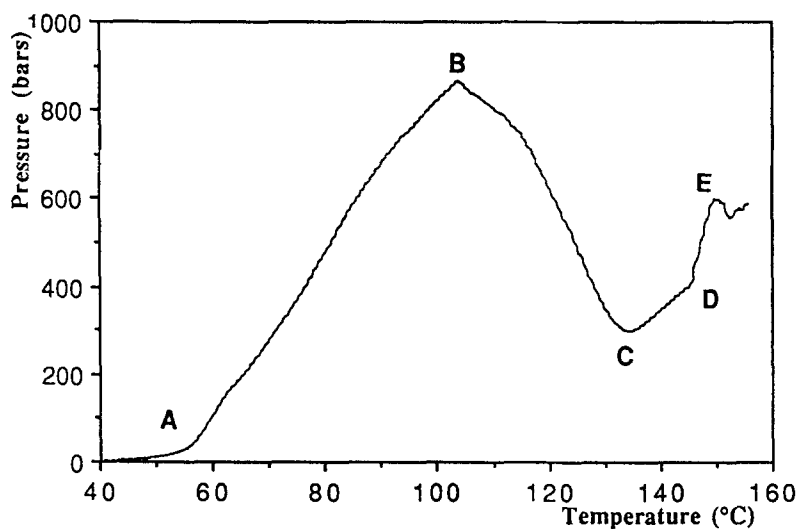


Fig. 2 Thermobarogram of Ca-Mg polyphosphate coacervate

- an important pressure decrement (part B-C),
- a new pressure increment (part C-E) including two parts (C-D and D-E) with different slopes.

For Ca-Na gel, thermobarograms exhibit a pronounced similarity to coacervates's ones. However, the pressure decrease (part BC) is much more spread versus temperature, for gel (about 60°) than for coacervates (about 15 to 25°); moreover, these pressure decreases, versus the temperature, are irregular for gel.

For both gel and coacervates, after a high temperature run (>180°), opening of the cell at room temperature shows that the sample is in a solid state.

Taking account of DSC curves [4] and the infrared spectra [11], the following interpretation for the thermobarograms of coacervates is proposed:

- Part A-B: expansion of the sample under temperature effect which induces a strong pressure increment;
- Part B-C: release of the 'free water', initially included in the tightly coiled chains, with a strong pressure decrease issue from a strong volume decrement;
- Part C-E: hydrolysis of the metaphosphates chains in orthophosphates according to the mechanism proposed by Watanabe [12]; the separation in two parts of that region of the thermobarogram is still unexplained.

Generally, the physico-chemical transformations ("free water" release, hydrolysis) occur at higher temperature for the Ca-Mg coacervates than for the Ca-Na one; previously, such behaviour has already been observed by DSC [4].

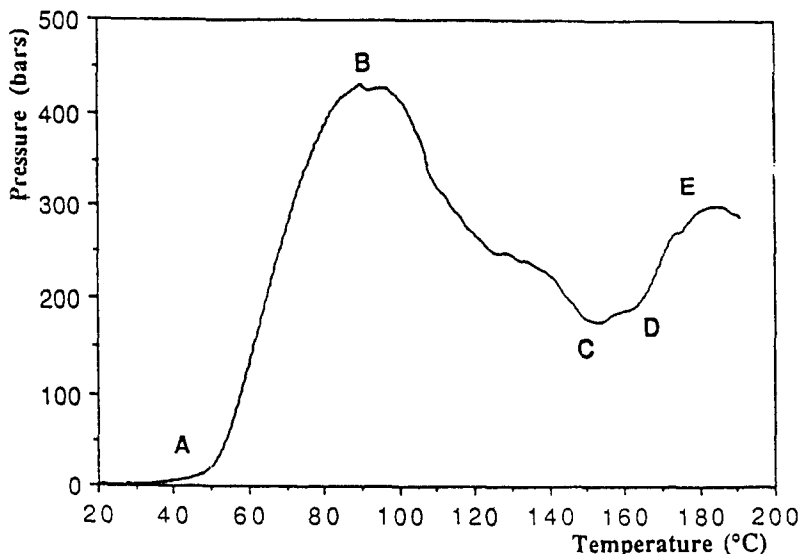


Fig. 3 Thermobarogram of Ca-Na polyphosphate gel

For gels, the interpretation is similar to the case of coacervates. The more important spread of the release of "free water" can be explained by a more rigid network of micro-domains (gel) than for the coiled packing (coacervates); domains (gel) than for the coiled packing (coacervates); however, no explanation can be just now given relative to the irregularity of the pressure change during that transformation.

## Conclusion

The physico-chemical transformations of polyphosphates in gels and coacervates states were investigated under pressure by thermobarometric analysis. In every case, the same general shape is obtained for the thermobarograms. The most important result is that the release of the "free water", is detected by an important and progressive decrement of pressure issue from a strong volume decrement. At higher temperature, the hydrolysis of the systems leads to another pressure increment. Such experiments show that the chemical reactions can be studied under pressure by thermobarometric analysis. Moreover, for the first time, negative volume changes for a transformation obtained by increasing the temperature has been able to be observed by thermobarometric analysis. However, a more perfect analysis of the thermobarograms for a better understanding of the phenomena occurring under pressure needs now a theoretical modelization.

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**Zusammenfassung** – Mittels thermobarometrischer Analyse wurden Gele und Coacervate von Polyphosphat-Systemen ( $xMO - y P_2O_5 - z CaO - n H_2O$ , mit  $M = Na$  oder  $Mg$ ) untersucht und auf physikochemische Umwandlungen bis 1000 bar geprüft. Die generelle Form

der Thermobarogramme ist in allen Fällen dieselbe. Zuerst wird ein starkes Druckinkrement beobachtet, das auf die Probenexpansion unter Temperatureinfluss zurückgeht. Dann, zwischen 100 und 110°C, wird die Abgabe von freiem Wasser durch eine ausgeprägte und progressive Abnahme der Druckwirkung infolge starker Volumabnahme angezeigt. Bei höherer Temperatur wirkt sich die Hydrolyse des Systems in Form von Druckinkrementen aus. Diese Experimente belegen erstmals, dass durch thermobarometrische Analyse physikochemische Umwandlungen leicht zu untersuchen sind. Darüber hinaus ist es zum ersten Mal gelungen, eine mit zunehmender Temperatur bei einer Umwandlung eintretende negative Volumänderung thermobarometrisch zu beobachten.