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PHYSICO-CHEMICAL TRANSFORMATIONS UNDER PRESSURE OF COACERVATES AND GELS OF POLYPHOSPHATES

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The physico-chemical transformations of gels and coacervates of polyphosphates (x MO - y P_2O_5 - z CaO - n H_2O, where M = Na or Mg) were investigated under pressure by thermobarometric analysis. In every case, the thermobarograms had the same general shape; the transformations were identified by using the infrared spectra of the products obtained at various stages of the analysis and the thermograms obtained by differential scanning calorimetry. The most important result was that the free water release can be detected via a considerable and progressive decrease in pressure resulting from a strong volume decrease. At higher temperature, the hydrolysis of the systems leads to pressure increases.

Gels and coacervates of polyphosphates are of increasing interest as concerns coverings used in protection against oxidation [1]. Such systems are colloidal states obtained from solutions of polyphosphate macromolecules [2]. In coacervates, the polyphosphate chains are tightly coiled, keeping "free water" included [3]. In gels, the presumed structures fit microdomains, the chain packing including the "free water" [3]. In both systems, "bonded water" exists. On increase of the temperature of these systems, very complex physico-chemical processes, such as free water release, hydrolysis and thermal condensation, occur [3]. Although the thermal behaviour of such systems under atmospheric pressure is now beginning to be understood [2–4], to our knowledge nothing has been done as regards higher pressure studies. Following our investigations by thermobarometric analysis of the behaviour under pressure of the phase transitions (first and second order or glass tran-

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sitions) of organic compounds (monomers or polymers) [5–10], we have now investigated the behaviour under pressure of the chemical transformations in solutions of mineral polymers, i.e. gels of calcium-sodium polyphosphates and coacervates of both calcium-sodium and calcium-magnesium polyphosphates. For their understanding, the experimental results were compared with differential scanning calorimetry data. In order to identify the products obtained at various stages of the thermobarometric analysis, infrared spectra were recorded after the samples had been heated to various temperatures and then restored to room temperature and atmospheric pressure.

Experimental

Material

The studied compounds were

$$x\,\mathrm{MO} - y\,\mathrm{P_2O_5} - z\,\mathrm{CaO} - n\,\mathrm{H_2O}$$

where M = Na or Mg; such systems can exist in both gel and coacervate states under atmospheric pressure, depending on the experimental elaboration [2]. The polyphosphate coacervates are prepared by adding a 2 M $Ca(NO_3)$ solution to a 0.5 M Na polyphosphate Graham salt solution. Ca-Mg coacervate is obtained through Na-Mg ion-exchange via a salting-out effect. Ca phosphate gel is prepared by adding a CaO solution to the Graham salt solution. Details on the preparation of these coacervates and gels have been given elsewhere [2].

For both Ca-Na and Ca-Mg coacervates, the aim was to extend to higher pressure the known results previously obtained by means of differential scanning calorimetry [3]. For gels, we have investigated only the Ca-Na system, to compare its pressure behaviour with that of the coacervate.

Methods

Thermobarometric analysis

Pressure studies were carried out in a Numerical Scanning Metabolemeter (M. A. B. O2 A-20, M. T. M. LEADER). The measurements consisted in recording the pressure of a sample enclosed in a weakly dilatable cell versus temperature [5, 8]. The samples were initially in the fluid phase and filled the whole cell (20 mm^3). The experiments were performed at constant mass, and in the temperature range 30–180° and the pressure range 0–1 kbar, at quasi-constant volume [8]. The thermobarograms for the three studied systems were plotted at a heating rate of 2 deg/min.

Infrared analysis

Infrared analyses were performed on the Ca-Na coacervate at atmospheric pressure with a F. T. I. R. M-1730 spectrophotometer (Perkin Elmer). Transmission spectra were recorded at various stages of the thermobarometric analysis, after the sample had been heated to various temperatures (and then various pressures) and restored to room temperature.

Thermal analysis

The calorimetric behaviour of the Ca-Na coacervate was investigated on a differential scanning calorimeter (D. S. C. 111, Setaram). A freshly prepared coacervate was sealed in an inox crucible. The runs were carried out at a heating rate of 5 deg/min.

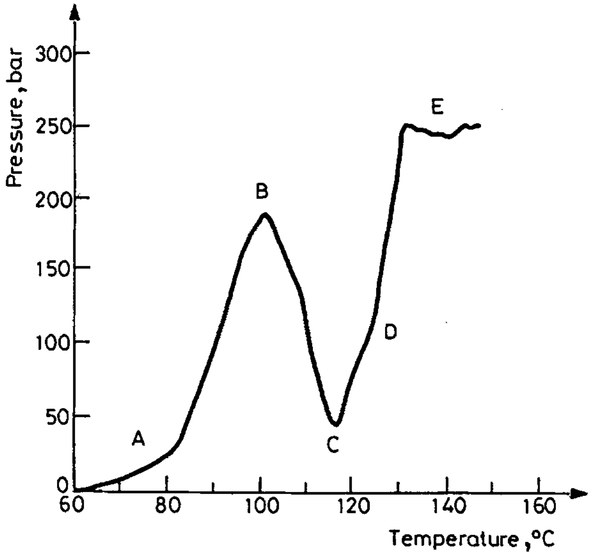

Fig. 1 Thermobarogram of Ca-Na polyphosphate coacervate

Results and discussion

Thermobarometric analysis

Examples of thermobarograms obtained for the coacervates of calcium-sodium and calcium-magnesium and for the gel of calcium-sodium are reported in Figs 1–3, respectively. For each of the three systems, numerous samples were studied, and the results were perfectly reproducible. The general features of the thermobarograms for Ca-Na and Ca-Mg coacervates (Figs 1 and 2) are similar. They always exhibit:

- a significant pressure increase (part A-B),
- a significant pressure decrease (part B-C),
- a new pressure increase (part C-E), including two parts (C-D and D-E) with different slopes.

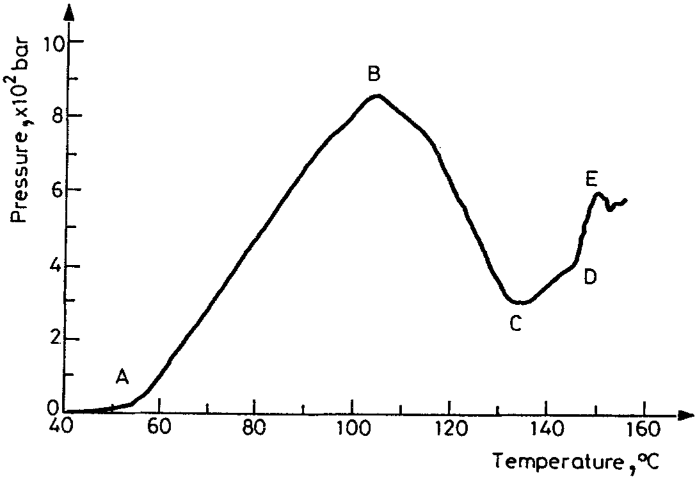

Fig. 2 Thermobarogram of Ca-Mg polyphosphate coacervate.

Before point C is reached, the thermobarograms obtained from successive heating cycles, are perfectly reproducible. Thus, no irreversible physico-chemical transformation has occurred before point C.

For the Ca-Na gel, the thermobarogram exhibits great similarity to that of the coacervate. However, the pressure decrease (part B-C) is much more spread versus temperature for the gel (about 60 deg) than for the coacervate (about 15 to 25 deg); moreover, these pressure decreases versus temperature are irregular.

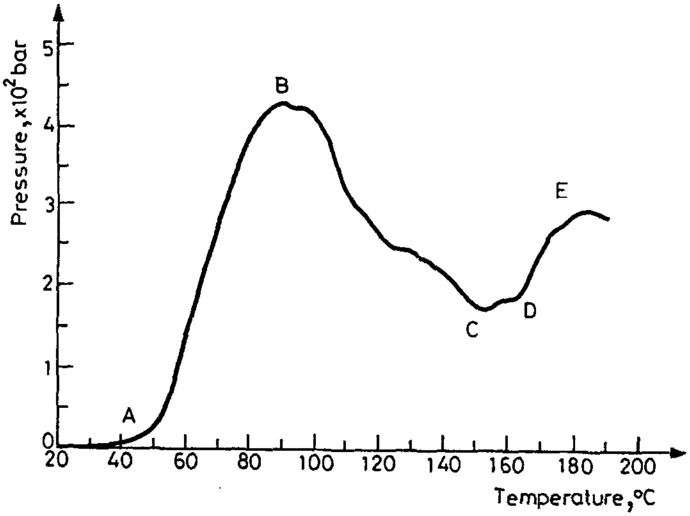

Fig. 3 Thermobarogram of Ca-Na polyphosphate gel

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

Infrared spectra

Figure 4 gives infrared spectra obtained on Ca-Na coacervate: 4a: on a fresh sample, 4b: at point B, 4c: at point C, 4d: near point D, and 4e: near point E. The polyphosphate chains are characterized by the strong 1270 cm^{-1} band due to the $\nu_s(PO_2)$ vibrations. The 1100, 1020, 880 and 500 cm^{-1} bands are attributed to $\nu_{as}(PO)_2$, $\nu_s(POP)$, $\nu_{as}(POP)$ and $\delta(PO_2)$, respectively.

After point C in the thermobarogram, the IR spectra of the cooled samples show significant changes. The 1160, 1076 and 970 cm^{-1} bands are characteristic of non-condensed phosphates. Moreover, the broad absorption in the $\nu(OH)$ region (2950 cm^{-1} indicates that the polyphosphate chains turn into hydrogenphosphates. Consequently, point C corresponds to the beginning of polyphosphate chain hydrolysis.

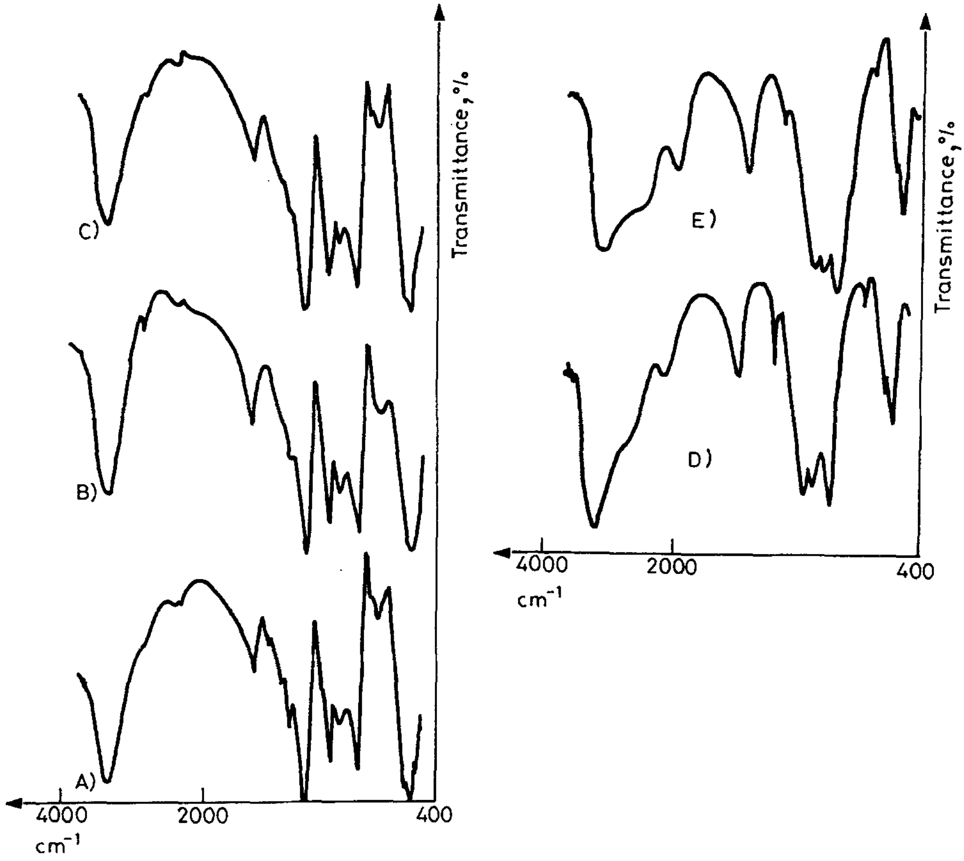

Fig. 4 Infrared spectra of Ca-Na polyphosphate coacervate obtained at various stages of the thermobarometric analysis after return at room temperature and atmospheric pressure

DSC measurements

The DSC curve obtained at atmospheric pressure for a fresh Ca-Na coacervate is presented in Fig. 5. It exhibits an exothermic peak between 90 and 125°, corresponding to hydrolysis of the polyphosphate chains [3–4]. Then, a weakly endothermic peak is observed near 140° ; this could correspond to "bonded water" release [4].

Interpretation of thermobarograms

Taking into account the of IR measurements (Fig. 4), hydrolysis can be detected only after point C in the thermobarograms. In the DSC curves, the

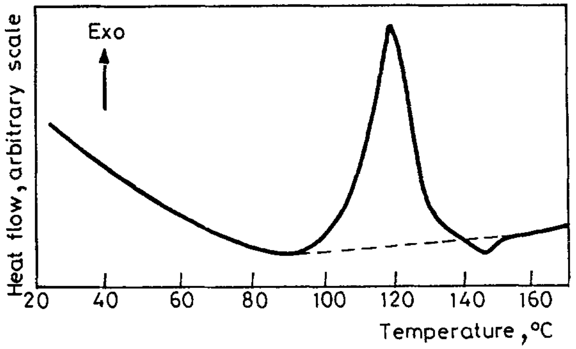

Fig. 5 Curve of fresh Ca-Na polyphosphate coacervate under atmospheric pressure

hydrolysis occurs with a strong positive enhalpy of reaction (Fig. 5) at constant pressure; at constant volume, therefore, this transformation should be detected in the thermobarograms as a considerable pressure change [11]. Moreover, owing to the pressure dependence of the transformation temperature, hydrolysis should be detected at higher temperature in the thermobarograms than in the DSC curves. However, to our knowledge, no experimental or theoretical data are available as concerns the slope $\left(\frac{dP}{dT}\right)$ and the pressure change ΔP during such a transformation, which limits the exploitation of the thermobarometric measurements.

Thus, we propose the following interpretation for the thermobarograms of coacervates:

Part A-B: expansion of the sample in response to the temperature change, which induces a strong pressure increase;

Part B-C: release of the "free water" initially included in the tightly coiled chains, with a strong pressure decrease resulting from a strong volume decrease;

Part C-E: hydrolysis of the metaphosphate chains in the orthophosphates according to the mechanism proposed by Watanabe [12]; the separation of the thermobarogram into two parts in that region is still unexplained.

Generally, the physico-chemical transformations ("free water" relase, hydrolysis) occur at higher temperature for the Ca-Mg coacervate than for the Ca-Na coacervate; previously, such behaviour was observed by means of DSC [4].

For gels, the interpretation is similar as in the case of coacervates. The more significant spread of the release of "free water" can be explained by a more rigid network of microdomains (gel) than for the coiled packing (coacervate); however, no explanation can yet be given as regards the irregularity of the pressure change during this transformation.

In order to confirm these interpretations, a theoretical modelling of the thermobarograms for systems exhibiting chemical reactions is under way [11]; experimental verification will subsequently be attempted on mineral polymers exhibiting individually "free water" release and hydrolysis phenomena.

Conclusion

The physico-chemical transformations of polyphosphates in gels and coacervates were investigated under pressure by means of thermobarometric analysis. In every case, the same general shape was obtained for the thermobarograms. The physico-chemical transformations which occurred in the course of the pressure studies were identified via the infrared spectra of the products obtained at various stages of the analysis and the thermograms obtained by differential scanning calorimetry on fresh samples. The most important result is that the release of the "free water", is detected as a considerable and progressive decrease in pressure resulting from a strong volume decrease. At higher temperature, the hydrolysis of the systems leads to another pressure increase. Such experiments show that 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 observed by means of thermobarometric analysis. However, a more perfect analysis of the thermobarograms for a better understanding of the phenomena occurring under pressure now needs a theoretical modelling.

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Zusammenfassung — Mittels thermobarometrischer Analyse wurden die physikalisch-chemischen Umwandlungen von Gelen und Koazervaten von Phosphaten der Zusammensetzung $x\mathrm{MO}\cdot y\mathrm{P_2O_5}\cdot z\mathrm{CaO}\cdot n\mathrm{H_2O}$ (mit M = Na oder Mg) unter Druck untersucht. Die Thermobarogramme hatten in jedem Falle den gleichen Verlauf; die Umwandlungen wurden mittels von Infrarotspektren der bei verschiedenen Stufen der Analyse erhaltenen Produkte sowie der durch DSC erhaltenen Thermogramme identifiziert. Das wichtigste Ergebnis bestand darin, das die Abgabe des freien Wassers an Hand einer beträchtlichen und progressiven Druckabnahme erkannt werden konnte, die sich aus einer starken Volumenabnahme ergab. Bei höheren Temperaturen führt die Hydrolyse des Systemes zu einer Druckerhöhung.