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Structure of zirconium phosphate gels produced by the sol–gel method

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Abstract. Several zirconium phosphate (ZrP) gels of various water contents produced by a sol–gel method were investigated. They were found to be the polymer-class gels using the method of small-angle neutron scattering. X-ray diffraction analysis revealed that their solid-phase framework was formed from branched fragments (layers and blocks) of α -ZrP crystal structure. These gels are strongly fluctuating systems when they are on the scale of $r < \xi$. Their fluctuation character is shown to be described by two parameters: a correlation radius ξ and a fractal dimension D . It was found that $\xi \approx 2.5$ nm and almost did not depend on the water content and that D increased from 1.4 ± 0.25 to 2.6 ± 0.20 when the water content decreased from 50% to 0% as the gels were dried to a temperature of 105 °C. Simultaneously, substantial shrinkage of granules, a decrease in porosity and ion-exchange capability, and formation of blocks from α -phosphate layers occurred with α decrease in the water of the hydrogel as it dried. A probable description of the evolution of the ZrP-gel structure with variation in the water content during drying is suggested on the basis of the data obtained.

1. Introduction

Zirconium phosphate (ZrP) gels are classified as inorganic cation exchangers of higher radionuclide selectivity from water solutions in the form of an amorphous, semicrystal or crystal structure [1–7] depending on the technique used for synthesis. However, the ZrP gels are of the same chemical composition irrespective of their degree of crystallinity. Their chemical composition is characterized by the stoichiometric P to Zr ratio of 2 relevant to its basic formula $\text{Zr}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ [2, 7, 8], where n depends on the drying method and the degree of dehydration.

The crystalline α -ZrP composition $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ is strictly stoichiometric and has a laminar structure [2, 6]. The α -ZrP layers consist of zirconium atoms located in the same plane and bonded with one another by the phosphate groups lying above and below the plane composed of zirconium atoms. The layers are packed into blocks, so that they form the structure of a monoclinic lattice with the following cell dimensions: $a = 0.9097$ nm, $b = 0.5307$ nm and $c = 1.6284$ nm; $\beta = 111.38^\circ$. The amorphous and semicrystalline ZrP gels have been considered by some workers [2, 8] to be formed from small crystalline α ZrP particles, and others [9–13] refer to them as polymer formations. The selective sorption properties of ZrP gels are affected by the crystallinity and degree of dehydration of the material [2, 8, 13–17]. Also, the latter characteristic strongly affects the exchange kinetics [14, 16, 18].

Ion-exchange and dehydration reactions in compounds based on α -ZrP of high crystallinity proceed with the formation of intermediate phases of stoichiometric content. That is well proved by the titration and dehydration [2, 6] curves. The ion-exchange reactions in the low-crystallinity compounds proceed with the formation of a row of continuous solid solutions and the dehydration reactions result in phases with an arbitrary number of moles of water. The speed of these reactions and the ion-exchange selectivity strongly depend on the crystallinity. Thus, as the degree of crystallinity is one of the most important structure characteristics of the ZrP gels, it determines their ion-exchange properties.

Usually, the degree of crystallinity is estimated from the size of the solid-phase particles forming the gel matrix [6]. The size can be calculated from the half-width of Bragg reflections in the gel's x-ray pattern [8, 14, 16, 17]. Another method of determining the degree of crystallinity is a comparison of the heats of formation of the solid phases of different specimens [19]. A specific surface value also described the crystallinity.

However, the degree of crystallinity does not fully characterize the gel's structure as it does not provide information on the correlation between the solid-phase parts, i.e. on the gel matrix surface.

A definition of some ZrP gel characteristics (specific surface, surface and volume conductivity) implies that the gel is formed from colloidal solid-phase particles having a well defined surface. However, it is known that at least two different types of gel are possible: polymer and colloidal gels. The former are produced by chemical linking of branched polymer clusters. The latter are three-dimensional non-porous solid-phase particles of small size. In our opinion, at the present time there do not appear to be any previously reported experimental data which can be used to specify and refer to the ZrP gels of the types mentioned above.

One of the experimental methods by which the gel can be classified as of the polymer or colloidal type more or less unambiguously is the small-angle scattering of neutrons or x-rays. In general, the power dependence of the small-angle intensity asymptotic $I(q \rightarrow \infty)$ to the momentum transfer $q (= 4\pi \sin \vartheta / \lambda$, where λ is the irradiation wavelength and ϑ is the scattering angle) [20] is typical for all gels:

$$I \sim q^{-n}. \quad (1)$$

For polymer-like objects the value of n can take a value within the interval $1 < n < 3$. Here, n coincides with the fractal dimension D . The value of D is a very important characteristic for such random objects as gels. For three-dimensional objects (such as colloidal particles with a rough or smooth interface), n is within the interval $3 < n \leq 4$. In this case, $n = 6 - D_S$, where D_S is the fractal dimension of the surface.

Thus, we can deduce the type of gel studied from an analysis of the asymptotic behaviour of the scattered irradiation intensity.

It should be noted that almost all structure investigations of ZrP gels have been performed on samples synthesized by precipitation methods (a gel method), which resulted in low-strength granules of an irregular form. Recently sol-gel methods have been extensively developed which allowed ZrP spherical granules [21–23] of sufficient strength to be produced. Such material can be used for various flow processes. However, the structure of such spherical-granule ion-exchangers have been investigated very little.

Our objective was to study the structure of ZrP gels synthesized by the sol-gel method using the combination of small-angle neutron scattering (SANS) and x-ray diffraction analysis. The task was to reveal the evolution of the structure and some properties of gels depending on their degree of dehydration.

2. Experimental details

ZrP samples of spherical-granule form were produced by a sol–gel method [22, 23]. The method consists of the following main stages: the production of a zirconium hydroxide sol by electrolysis of a zirconium oxychloride solution; sol drop dispersion into an ammonia solution, resulting in the formation of zirconium hydroxide gel spheres (i.e. gelatinization), washing of the gel spheres and treating them with a phosphoric acid solution (i.e. conversion) to transform the hydroxide into zirconium phosphate. The granules were partially transformed into a sodium form by treating them with a sodium hydroxide solution; then the electrolytes were washed off and the granules were subjected to chemical analysis. It should be noted that some of the hydrogen atoms were substituted by sodium atoms; this did not effect the gel structure. The product had the following stoichiometric content: $\text{Zr}(\text{H}_{0.75}\text{Na}_{0.25}\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ (atomic ratio of P to Zr, 2.0). The ZrP spherical granules were dried in air to attain the desired humidity and then tested. In total, eight samples of different dehydration levels were produced. Sample 8 was a xerogel dried at 105 °C to reach a constant mass. The bulk density and pore volume per unit solid-phase mass were determined by the method in [18]. The water loss determined the humidity after the sorbent was dried at 105 °C to reach a constant mass. The exchange static capacities for ammonia and strontium were determined in solutions of NH_4Cl (0.1 mol l⁻¹) and SrCl_2 (0.05 mol l⁻¹), respectively, at pH 7.0 and also per unit solid-phase mass of waterless sorbent.

X-ray patterns of all the samples were taken in a range of large scattering angles to determine the atomic structure and dimensions of the region of solid-phase gel coherent scattering.

The gel structure parameters were determined by measuring SANS at room temperature. The x-ray and SANS set-ups used for the investigations of the ZrP gels have been described in [24].

The dependence of the physical and chemical properties of the ZrP samples on the degree of dehydration are summarized in table 1. Gel spheres of the initial hydrogel have a humidity of 59.1 wt% and a pore volume of 1.44 cm³ g⁻¹, i.e. they are highly porous and permeable structures. When the gel spheres are dried, a substantial shrinkage of granule volume (4.3 times) is observed, followed by a bulk mass increase and a pore volume reduction with decrease in humidity. The ZrP xerogel (sample 8) became non-porous and impermeable to molecules of nitrogen, benzene and helium according to the adsorption data [25]. However, it swells and its volume increases in water vapour and water solution.

Table 1. Physical and chemical properties of ZrP samples.

Sample number	Material condition	Humidity (wt%)	Pore volume (cm ³ g ⁻¹)	Relative volume V_1/V	Capacity (mmol g ⁻¹)		Lattice parameter (nm)	Correlation parameter (nm)	Fractal dimension D
					NH_4^+	Sr^{2+}			
1	Hydrogel	59.1	1.44	1.00	5.68±0.02	2.69±0.12	—	1.9±0.3	1.40±0.25
2	Hydrogel	54.8	1.21	1.30	—	—	—	—	—
3	Hydrogel	44.1	0.79	1.82	—	—	—	2.5±0.3	1.50±0.25
4	Hydrogel	42.9	0.75	1.95	—	—	2.13	—	—
5	Hydrogel	37.2	0.59	2.30	—	2.15±0.10	2.10	2.2±0.3	1.6±0.2
6	Hydrogel	35.0	0.54	2.37	3.95±0.14	1.85±0.13	2.08	—	1.6±0.2
7	Air-dried gel	9.2	0.10	3.72	2.51±0.25	1.32±0.11	1.80	—	1.6±0.2
8	Xerogel	0.0	0.0	4.33	2.25±0.21	1.01±0.05	1.64	2.0±0.3	2.6±0.2

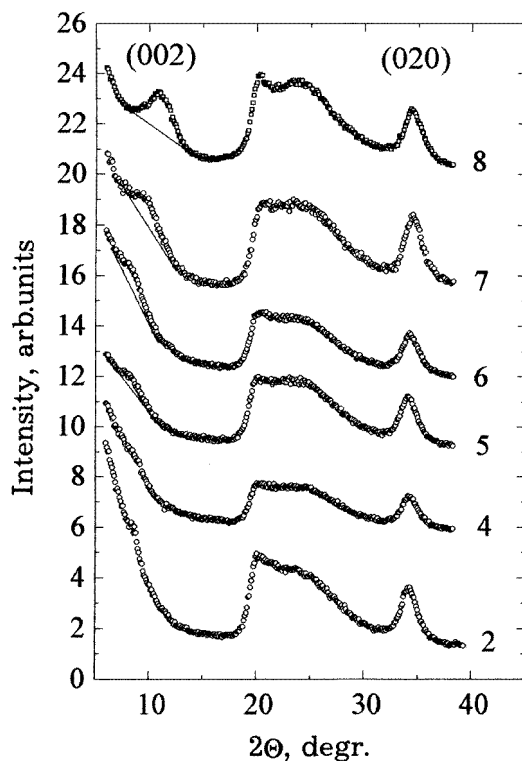


Figure 1. X-ray diffraction pattern of ZrP gels. The numbers are the sample numbers in table 1. The experimental curves are displaced arbitrarily on the vertical axis for convenience.

3. Results and discussion

X-ray patterns of ZrP samples are shown in figure 1. The relation to the relevant Bragg reflections of crystalline α -ZrP, are indicated in the x-ray patterns. A spectrum of crystalline α -ZrP may be obtained from [2, 4, 6] for comparison.

In general, broad lines and the absence of some reflections in the x-ray patterns prove the low crystallinity of the ZrP samples. Moreover, the reflection designated as (020) in figure 1, relevant to Zr atom ordering in flat areas, is present in all the x-ray patterns and does not change its position and size. This proves that the distance between Zr atoms in quasi-flat areas and their linear dimensions have not changed with the decrease in the amount of water during drying. Taking into account that Zr atoms in the plane (002) are linked through phosphate groups lying above and below that plane, then the data prove that fragments of two-dimensional layers of α -ZrP are present in the gel solid-phase framework. Figure 1 shows that there is no peak related to the (002) reflection in the x-ray pattern of sample 2. That peak was also not revealed in the patterns of samples 1 and 3; these patterns are not shown here. The (002) peak is seen in the pattern of sample 4 as a diffuse line with a half-width of the order of 4° . The peaks of samples 5–8 are shifted to larger angles, the peak half-width decreases and its intensity increases with a decrease in the amount of water. The (002) reflection in crystalline α -ZrP is known to be related to the distance between the Zr atom layers; therefore it can be concluded that the solid-phase framework of the gels 1–3 is formed by fragments of two-dimensional layers of α -ZrP and there are blocks

of packed layers in samples 4–8 which are similar to the laminated structure of α -ZrP. Also the distance between layers decreases with increase in the degree of dehydration of ZrP gel (see table 1, lattice parameter c) and for the xerogel the value of c approaches that of the elemental cell of α -ZrP.

An approximate estimation of the mean dimension of two-dimensional layers relevant to the (020) peak shows that all samples have the same value of this dimension, namely 5.0 ± 0.1 nm. At the same time the size of the coherent scattering area relevant to the (002) peak changes monotonically and similarly with a change in humidity and gel shrinkage and is 1.6–2.1 nm for samples 4–8, i.e. the blocks mentioned above consist of two to three layers.

As can be seen from table 1, the initial hydrogel has a high ion-exchange capacity for both cations NH_4^+ and Sr^{2+} . The solid-phase capacity decreases during drying, i.e. the xerogel sorption capability is 2.5 times lower than that of the initial hydrogel. A similar tendency was observed in [16, 18]. A decrease in the Ca^{2+} exchange capacity due to the decrease in the amount of water in ZrP is referred to in [18] as due to a reduction in the pore space and narrowing of pores. As is seen from table 1, the distance between ZrP layers is reduced during the gel is dried; this is proved by the change in the lattice parameter c , finally causing some monohydrophosphate ion groups to be inaccessible for cation exchange.

Figure 2 presents the SANS intensity data in the range $q = 0.5\text{--}4 \text{ nm}^{-1}$ for ZrP gel samples. The fact that the experimental points fit the straight line quite well indicates the scattering power law (1) and makes it possible to define the numerical value of n from the slopes of the straight lines. Here $n < 3$ and the index coincides with the fractal dimension.

Figure 3 shows the angle dependences of the SANS intensities in the range $q = 0.06\text{--}1 \text{ nm}^{-1}$. The solid curves were obtained from the following theoretical relationship:

$$I(q) = \frac{A \sin[(D-1) \tan^{-1}(q\xi)]}{q\xi(1 - q^2\xi^2)^{(D-1)/2}} \quad (2)$$

where D is the fractal dimension, ξ the correlation length and A a constant.

Equation (2) can be obtained by substitution of $g(r)$ in the form [26]

$$g(r) \sim r^{D-3} \exp(-r/\xi) \quad (3)$$

into the well known expression

$$I(q) \sim \int_0^\infty r^2 g(r) \frac{\sin(qr)}{(qr)} dr \quad (4)$$

which relates the intensity of scattered neutrons to the correlation function $g(r)$. Equation (3) was suggested in [26] to describe a volume fractal structure of finite size. Here $g(r)$ takes into account the space dependence of the density correlation of the ZrP gel matrix on the distance $r < \xi$. Equation (3) almost coincides with the function describing pair correlations in polymer gels [27]. According to [27] for chain polymer gels, $3 - D = 4/3$, which means that $D = 5/3$.

For $q \rightarrow \infty$ the asymptotic behaviour of equation (2) gives the expression $I(q) \sim q^{-D}$, which coincides with equation (1), when $D = n$. Thus equation (2) satisfactorily describes the experimental curves of SANS for ZrP hydrogels within the entire interval of scattering angles (figure 3). Therefore, it can be concluded that the fractal geometry concept is applicable to the gel structure analysis. The numerical values of the fractal dimension D and of the correlation radius ξ were determined by the method of best fit of the curve from equation (2) and the experimental points in figure 3. The values of correlation length and fractal dimension for samples 1, 3, 5 and 8 determined by that method are shown in table 1. The fractal dimensions for samples 1, 3, 6, 7 and 8 were obtained from the slopes

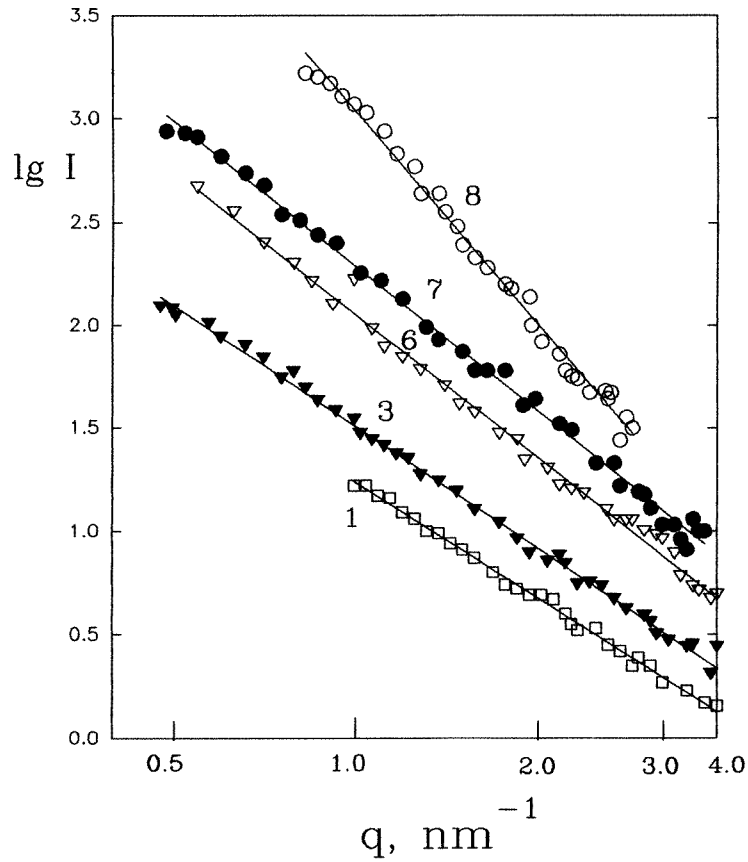


Figure 2. SANS data for ZrP gels on a log–log scale. The numbers are the sample numbers in table 1. The experimental points are arbitrarily displaced on the vertical axis.

of the straight lines in figure 2. These data are also shown in table 1. The values of D for samples 1, 3 and 8 determined by both methods agree with each other within the accuracy of the experiment.

Large errors in defining the parameters D and ξ account for both the large incoherent scattering background in the water present in the samples, and the relatively small interval of q -values in which equation (2) and the experimental data were fitted. In spite of the substantial uncertainty in the value of the parameter $D = n$, it can certainly be studied that it does not exceed the value of $n = 2$ for samples 1, 3 and 5. This allows us to classify the ZrP samples studied as polymer-class gels. This conclusion does not contradict the x-ray diffraction data if we assume that the matrix of the solid phase consists of packed fragments of an α -ZrP layer, when they are of a branched type. Unfortunately, the noticeable error in the definition of D does not allow us to state unambiguously that the measured values of D for the samples containing a large amount of water equals $5/3$ as obtained for the polymer-type gels in [27].

The important conclusion from our investigation is the compaction of the gel's framework in our samples on decrease in their water content. This resulted in an increase in the fractal dimension D from 1.40 ± 0.25 for the sample with maximum water content,

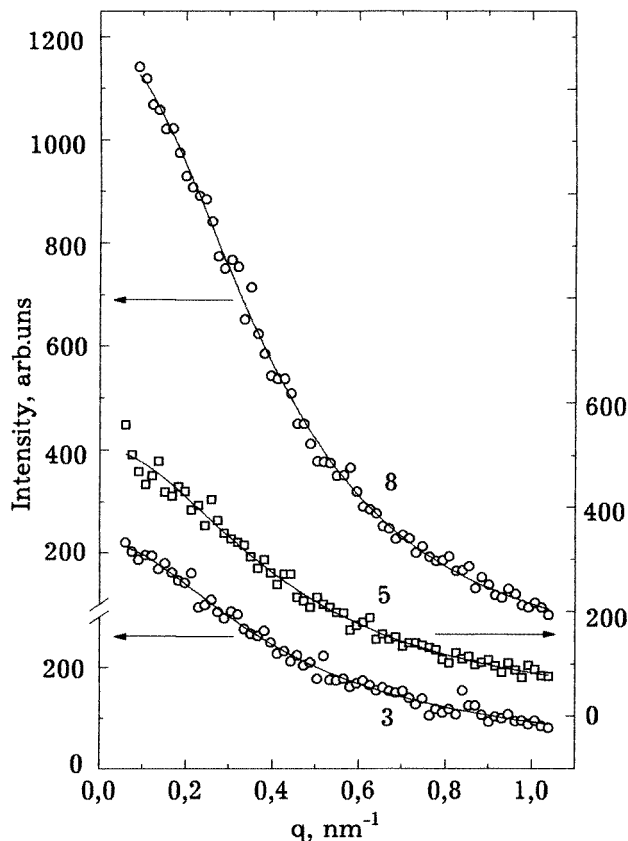


Figure 3. Angle dependence of SANS intensity for ZrP gel samples. The neutron count for 1000 s is presented. The solid curves were calculated from equation (2) in the text. The numbers are the sample numbers in table 1.

to 2.60 ± 0.20 for sample 1 dried at 105°C .

Thus we can describe the ZrP gel structure evolution in the process of drying based on the facts found (the increase in the fractal dimension with decrease in the water content) and x-ray diffraction data mentioned above.

The ZrP gels with the approximately 50 wt% H_2O are formed by branched fragments of crystalline α -ZrP layers, which are intrapacked, to form a framework with typical distances between layers approximately equal to ξ . At distances $r < \xi$ the density fluctuations are very strong, and can be described by the fractal dimension D (equation (3)). In this case, D equals approximately 1.5, indicating the one-dimensional framework of the fractal structure. At distances $r > \xi$ the gel is homogeneous. During drying, the gel is affected by capillary compression forces [28] and its structure forms branched blocks made up of several layers, without a clearly restricted interface.

A block or sheet-type [20] structure seems to be realized in specimen 8 with $D = 2.60$. A further increase in the fractal dimension D can be assumed for temperatures above 105°C during ZrP drying.

As this polymer gel is an ion exchanger, it should be a polyelectrolyte. In conclusion, we shall briefly discuss the experimental data on the ZrP gel in terms of polyelectrolyte

theory. For diluted linear polymer electrolytes it is predicted in [29] that

$$I(q) \sim S(q) \sim 1/q\xi \quad q > \xi^{-1} \quad (5)$$

where $S(q)$ is the Fourier image of the correlation function $g(r)$ (3). According to (5), polyions in a diluted solution are in the form of rigid extended rods. This is equivalent to $D = 1$ in equation (4).

For concentrated solutions of polyelectrolytes or in charged gels the situation is not so clear. However, De Gennes *et al* [29] considered the scattering law (5) to hold provided that the solution concentration is less than that required for condensation of counterions to occur.

On the other hand, the statistical theory of charged macromolecules [30] states that their conformational properties are intermediate between those of unswollen statistical balls ($D = 2$) and rigid rods ($D = 1$). This implies that $D = 3/2$ for the charged gels. It is known that the neutral polymer gel theory predicts that $D = 5/3$.

The values obtained for the fractal dimension D , especially for specimens 1, 3 and 5, are closer to $3/2$ than to $5/3$. However, choosing between these values is difficult because the definition of D is not sufficiently accurate. It seems possible to increase the accuracy of measuring D in the experiments on ZrP gels synthesized in the presence of heavy water.

The theory of polyelectrolytes allows us to comprehend qualitatively what causes ZrP gels to swell when saturated by water (see table 1). According to the theory in [30] the square of the linear polyelectrolyte swelling coefficient is proportional to $I_0^{-2/3}$ (where I_0 is the ionic force). Swelling of a gel increases with increasing dilution of the solution, because a decrease in the polyelectrolyte concentration suggests a decrease in the ionic force. Thus, the interpretation in terms of polyelectrolyte theory is beneficial to the analysis of ZrP gel properties.

4. Conclusion

By the SANS method it was found that ZrP gel samples of different humidities are classified as polymer-class gels and do not have a well defined interface between solid and water phases. The x-ray diffraction data revealed that the solid-phase framework of gels is formed by branched fragments of crystalline structure of α -ZrP (layers and blocks).

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