Influence of anions on the kinetics of hydrogen/sodium ion exchange in a crystalline acid zirconium phosphate

Vitalii Yu. Kotov,[a] **Irina A. Stenina**[a] **and Andrei B. Yaroslavtsev***[b]

[a] *Higher Chemical College, Russian Academy of Sciences, 125047 Moscow, Russian Federation*
[b] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 117907 Moscow, Russian Federation. Fax: +7 095 954 1279*

The rates of ion exchange in an acid zirconium phosphate in the presence of different sodium salts solutions and the diffusion coefficients were found to increase in the sequences $I^- < Br^- < Cl^-$ and $ClO_4^- < NO_3^- < SO_4^{2-}$; this phenomenon was explained by different mechanisms of defect formation.

The rate-controlling step for the majority of solid-state reactions is the diffusion of cations through the product layer.[1] The ionic diffusion within the bulk also plays a decisive role in various ion-exchange reactions. These reactions are most reliable because it is very easy to control changes in the reagent concentrations in the liquid phase. Recently, a method for determination of diffusion coefficients was proposed on the basis of studying the kinetics of ion exchange.[2] It was found using this method that the diffusion coefficients of cations in the products of acid zirconium phosphate (α-ZrP) exchange [$Na_2Zr(PO_4)_2\cdot 3H_2O$] significantly depend on the pH values of the solution in contact. It was concluded that proton defect migration is a rate-controlling step.[3] Anions present in solution can also take part in defect formation at the crystal surface and so affect the kinetics of ion exchange.

Crystalline acid zirconium phosphate was synthesised by the well-known procedure.[4] The substance was washed with water, treated in an ultrasonic bath to degrade agglomerates and then sieved. The fraction of 0.125–0.25 mm was used for the kinetic investigation. Potentiometric titration was made with an 'Elchim' pH meter. $Zr(HPO_4)_2\cdot H_2O$ was equilibrated with 0.4 M NaCl, NaBr, NaI, $NaClO_4$, $NaNO_3$ and 0.2 M Na_2SO_4 solutions at 302±1 K. Portions of a 0.1 M NaOH solution were added step by step, and pH was measured every 3 s. After equilibrium was reached, the next portion of the alkali was added. The solution was intensely stirred during the experiment.

The exchange in α-ZrP takes place by the migration of solid–solid interfaces between the two phases $Zr(HPO_4)_2\cdot H_2O$ and $NaHZr(PO_4)_2\cdot 5H_2O$ or $NaHZr(PO_4)_2\cdot 5H_2O$ and $Na_2Zr(PO_4)_2\cdot 3H_2O$.[5] Thus, the ion exchange at different steps can be described by the following equations:

$$Zr(HPO_4)_2\cdot H_2O + Na^+ + 5H_2O \rightleftharpoons NaHZr(PO_4)_2\cdot 5H_2O + H_3O^+ \quad (1)$$

$$NaHZr(PO_4)_2\cdot 5H_2O + Na^+ \rightleftharpoons Na_2Zr(PO_4)_2\cdot 3H_2O + H_3O^+ + H_2O \quad (2)$$

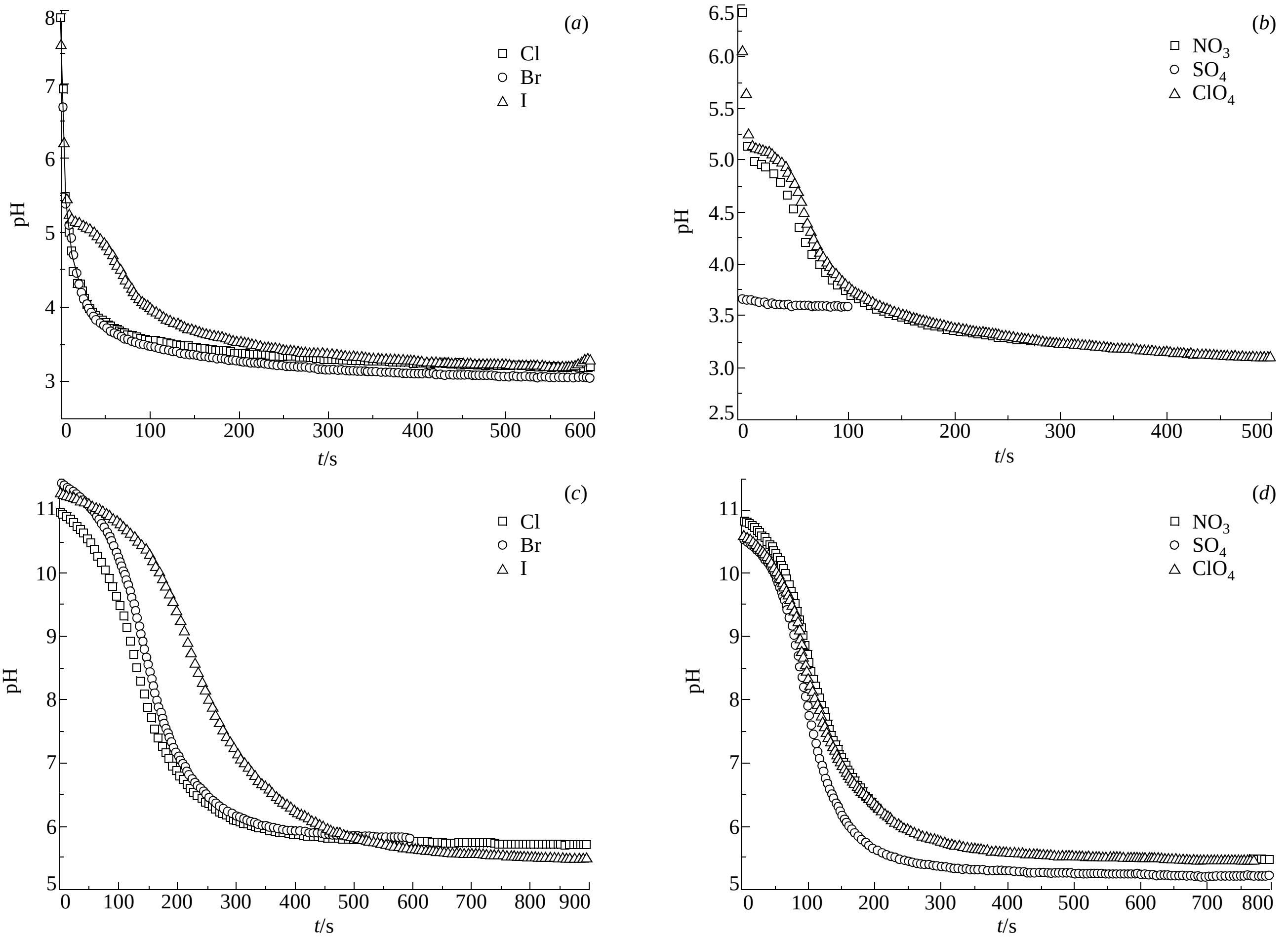

Figure 1 pH as a function of time: (*a*) and (*b*) I stage, the degree of exchange 58–77%, (*c*) and (*d*) II stage, the degree of exchange 17–36%; (*a*) and (*c*) in presence of NaCl, NaBr and NaI solutions, (*b*) and (*d*) in the presence of $NaClO_4$, $NaNO_3$ and Na_2SO_4 solutions.

The typical time dependence of pH values for the process examined is shown in Figure 1. At the beginning of the first step of exchange, the pH values sharply decreased and rapidly attained a plateau [Figures 1(*a*) and (*b*)]. For the first stage (conversion <50%), the pH–time plot exhibits an inflection point at pH values close to that for the equilibrium point of the second stage [Figure 1(*c*)]. This phenomenon is due to the formation of a nonequilibrium disubstituted phase [$Na_2Zr(PO_4)_2 \cdot 3H_2O$] at higher pH values. The low diffusion coefficients in this phase lead to inhibition of the overall process. The presence of this phase was found by X-ray diffraction.[3] The further decrease in pH can occur only after redistribution of sodium ions and protons within particles according to the reaction

$$Zr(HPO_4)_2 \cdot H_2O + Na_2Zr(PO_4)_2 \cdot 3H_2O + 6H_2O \rightarrow 2NaHZr(PO_4)_2 \cdot 5H_2O \quad (3)$$

The kinetic curves obtained for the first stage of the exchange in the presence of an Na_2SO_4 solution differ from the others [Figure 1(*a*) and (*b*)]. After addition of NaOH, the pH values remain almost unchanged. This phenomenon is explained by low activity coefficients of hydrogen ions in the Na_2SO_4 solution, because the majority of protons was consumed by association with SO_4^{2-} anions. The calculated amount of HSO_4^- ions is much greater than that of the hydroxide ions added at the first stage of exchange. The monoexchanged phase is formed almost completely after equilibrium was reached with the Na_2SO_4 solution. Thus, the addition of the alkali leads only to neutralisation of acids in solution. This fact is responsible for small pH variation and short equilibration time during the first stage of exchange. In all cases, the nature of the anion does not affect the thermodynamics of exchange.

The apparent diffusion coefficients as functions of the pH of solutions were calculated according to the equation suggested in ref. 2. Because of the formation of the nonequilibrium disubstituted phase, only a narrow range of pH is available for the correct determination of the diffusion coefficients of cations for the first stage [Figure 2(*a*) and (*b*)]. At the second stage of exchange, the calculated diffusion coefficient is described by a more complex function of pH [Figure 2(*c*) and (*d*)]. The strong dependence of log *D* on pH and the independence of sodium ion concentration proves that the diffusion of proton defects in the ion-exchanger body is a rate-controlling step. The log *D*–pH curve can be divided into three almost linear portions corresponding to three different mechanisms of defect formation. The slopes of these curves are determined by the number of OH^- anions, which is necessary for the formation of one defect in solids (α). For example, in the pH range 9–11, defects can be formed according to the equation:

$$H_H + Na^+_{aq} + OH^-_{aq} \rightleftharpoons Na^{\bullet}_i + V'_H + H_2O \qquad (\alpha = 0.5) \qquad (4)$$

where the subscript H denotes the ion position in the crystal lattice, i denotes inerstitials, V denotes vacancies, and the superscripts $^{\bullet}$ and $'$ denote the positive and negative charges of defects in the solid, respectively. Only a dynamic processes of single defect formation without charge compensation at the surface can correspond to the $\alpha = 1$ or -1 values:

$$7 < pH < 9 \qquad H_H + OH^-_{aq} \rightleftharpoons V'_H + H_2O \qquad (\alpha = 1.0) \qquad (5)$$

$$5 < pH < 7 \qquad H^+_{aq} \rightleftharpoons H^{\bullet}_i \qquad (\alpha = -1.0) \qquad (6)$$

Thus, the main types of proton defects in α-ZrP are vacancies ($7 < pH < 11$) and interstitials ($5 < pH < 7$). Note that the calculated diffusion coefficient depends on the nature of anions in solution. Its values increase in the sequences: $I^- < Br^- < Cl^-$, $ClO_4^- < NO_3^- < SO_4^{2-}$ [Figure 2(*c*) and (*d*)]. The most significant change in its magnitude occurs on going from sulfate to nitrate. This

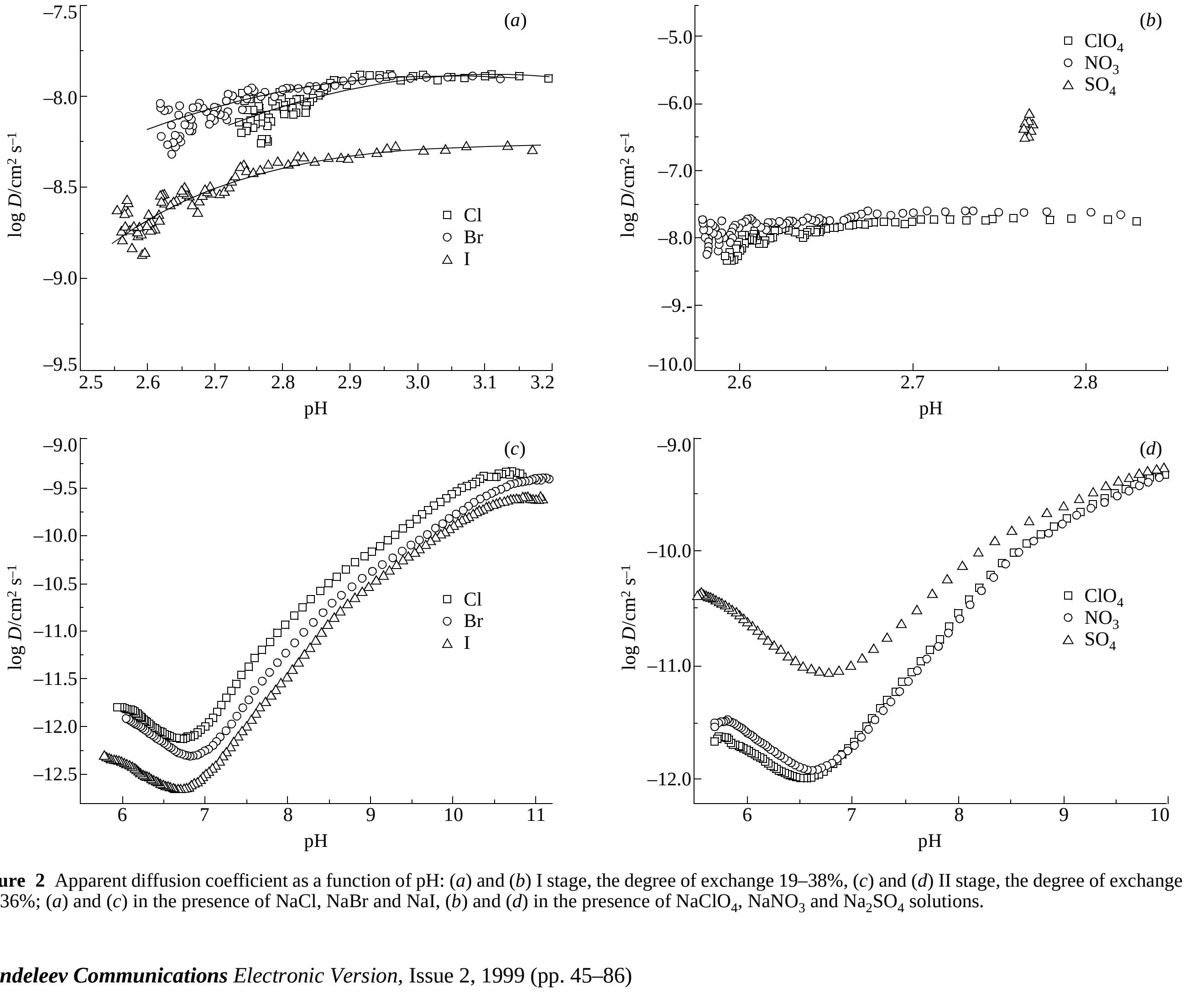

Figure 2 Apparent diffusion coefficient as a function of pH: (*a*) and (*b*) I stage, the degree of exchange 19–38%, (*c*) and (*d*) II stage, the degree of exchange 17–36%; (*a*) and (*c*) in the presence of NaCl, NaBr and NaI, (*b*) and (*d*) in the presence of $NaClO_4$, $NaNO_3$ and Na_2SO_4 solutions.

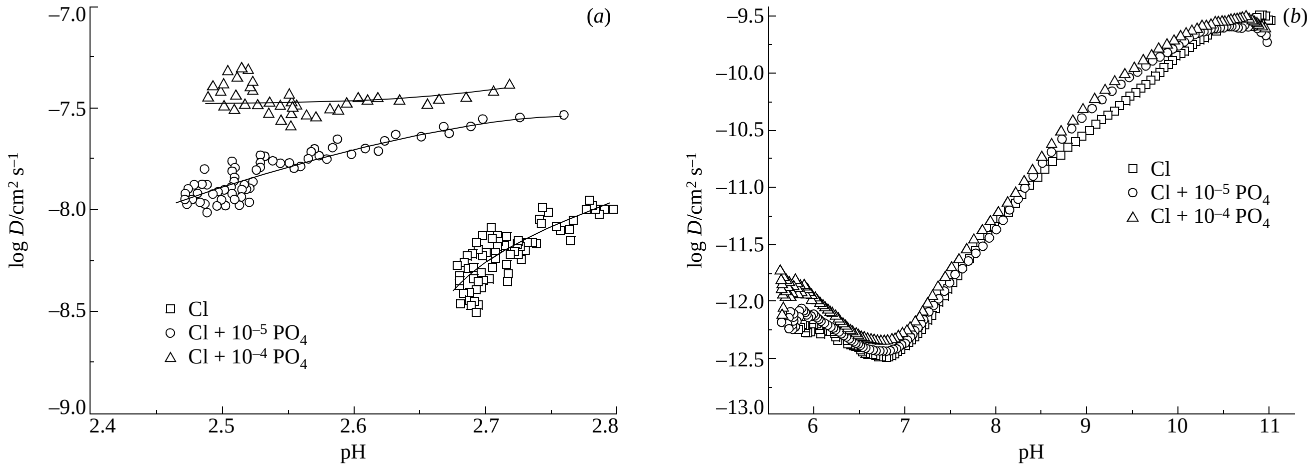

Figure 3 Apparent diffusion coefficient as a function of pH in the presence of a 0.4 M NaCl solution with trace amounts of 0, 10^{-5} and 10^{-4} M Na_2HPO_4 solutions: (*a*) I stage, the degree of exchange 0–19%, (*b*) II stage, the degree of exchange 36–55%.

fact can be explained only by the participation of anions in defect formation. Anions are unlikely movable through the lattice because of their large ionic radii. They can only take part in the defect formation at the surface. However, the defect concentration continuously changes in going from the ionite/ solution boundary toward the solid phase I/ solid phase II boundary because of diffusion. Thus, the total proton defect concentration in the sample and the average diffusion coefficient are determined by processes that take place at the crystal surface. Indeed, the surface density of the negative charges of anions decreases in the $SO_4^{2-} - NO_3^- - ClO_4^-$ and $Cl^- - Br^- - I^-$ sequences. The above sequence is determined by a decrease in the sorption ability of anions at the surface of double sodium zirconium phosphate. According to the data obtained, the additional defect formation in base solutions can be expressed by the equation

$$OH^-_{aq} + X^-_{aq} + (PO_4)_{PO_4} + 2H_H \rightleftarrows HPO^{2-}_{4\,aq} + X^{\bullet\bullet}_{PO_4} + 2V'_H + H_2O \quad (\alpha = 0.33) \qquad (7)$$

where X is an anion, the subscripts PO_4 and H denote the ion positions in the solid lattice. This equation describes the phosphate ions/X exchange on the particle surface. The formation of proton vacancies leads to charge compensation. For the solutions containing SO_4^{2-} ions, this process is most pronounced, and, according to another charge of the anion, this equation transforms to

$$SO^{2-}_{4\,aq} + (PO_4)_{PO_4} + H_H \rightleftarrows HPO^{2-}_{4\,aq} + (SO^{\bullet}_4)_{PO_4} + V'_H \quad (\alpha = 0) \quad (8)$$

Thus, the slope of log *D*–pH plots is the smallest in this case [Figure 2(*c*) and (*d*)].

At lower pH, the sorption of protons occurs at the interstitials on the crystal surface [equation (6)]. In acid solutions, it becomes easy because of anion sorption on the surface, which decreases the positive charge. The higher the sorption ability of anions, the greater the concentration of proton defects and the higher the diffusion coefficient. The influence of the nature of anions on the kinetics of ion exchange decreases with increasing pH. This is due to high concentrations of OH^- ions. In this range, their concentration becomes comparable to the concentration of the other anion in solution, and competitive processes take place.

The presence of a trace concentration of Na_2HPO_4 in NaCl solutions increases the diffusion coefficient also due to the large sorption ability of the anion [Figure 3]. This effect is more profound for the first stage [Figure 3(*a*)]. At the second stage, the sodium zirconium double phosphate remained in contact with the alkaline solution for a longer time, and hydrolysis can occur. As a result, the amount of phosphate ions added to the solution becomes comparable to that released in the hydrolysis. Thus, this effect becomes negligible [Figure 3(*b*)].

Thus, the data obtained suggest that the kinetics of cation exchange can be affected by the nature of anions present in solution. An increase in the sorption ability of anions leads to an increase in the diffusion coefficients of cations in the double sodium zirconium phosphate hydrate due to defect formation.

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