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Corresponding Member of the Academy of Sciences of the USSR B. P. NIKOLSKII, E. A. MATEROVA,

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Abstract

Full Text

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ION-EXCHANGE AND ELECTROCHEMICAL PROPERTIES OF ZIRCONYL PHOSPHATES

In recent years, inorganic ion exchangers have become widely used; among them zirconyl phosphate is the most promising. Various samples of zirconyl phosphates investigated by many authors (1-10) possess considerable exchange capacity, low swelling, and resistance to the action of radiation and high temperatures. The increased selectivity of zirconyl-phosphate ion exchangers toward a number of ions makes it possible to use them successfully for chromatographic separation. Zirconyl phosphates are obtained by the interaction of zirconium salts with phosphoric acid. The precipitates obtained have an indefinite composition, which depends on the state of zirconium in solution and on the relative amounts of zirconium and phosphoric acid in the solutions being mixed. The state of zirconium is determined by the degree of hydrolysis, which cannot be fixed precisely. Therefore not only the composition but also the properties of zirconyl-phosphate precipitates may vary within wide limits, a fact that is not always taken into account.

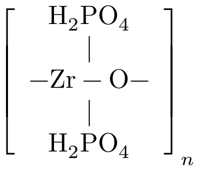
Fig. 1. Dependence of the exchange capacity Γ_{Na^+} (meq/g) of zirconyl phosphate on the composition of the sample for several pH values

The purpose of the present investigation was to clarify the influence of the composition of the zirconyl-phosphate precipitates obtained on their properties.

It is convenient to express the composition of a zirconyl-phosphate precipitate in the form of the molar ratio of zirconium and phosphorus oxides (K)

$$K = \mathrm{ZrO_2}\ \text{(moles)}/\mathrm{P_2O_5}\ \text{(moles)}.$$

For all precipitates obtained by the indicated method, $K \geqslant 1$. A sample with $K = 1$ corresponds to the following structure:



$$\left[\begin{array}{c} H_2PO_4 \\ | \\ -Zr-O- \\ | \\ H_2PO_4 \end{array}\right]_n$$

In samples with $K > 1$, hydroxyl functional groups apparently also enter the structure of zirconyl phosphate along with phosphate groups.

In the present work, samples of zirconyl phosphate of various compositions were obtained by precipitating zirconyl hydroxychloride, zirconium chloride, and zirconium nitrate with phosphoric acid at room temperature under conditions of intensive stirring. The order and rate of mixing of the reagents had no noticeable effect on the composition of the precipitate obtained. After mixing the solutions, the precipitates were left to settle overnight, then filtered off and washed with water until a negative reaction for the anion taken for precipitation of the zirconium salt was obtained, and dried at 120°.

Table 1

Sample No.	ZrO_2, mol/kg	P_2O_5, mol/kg	ZrO_2/P_2O_5	Concentration of acid in the zirconium salt solution	Composition of precipitate, $K = ZrO_2/P_2O_5$	Specific electrical conductivity, $ohm^{-1} \cdot cm^{-1}$	Volume capacity for Na^+ at pH 3, meq/g
1	0.2	1.0	1:5	$4M$ HCl	1.07	$2.02 \cdot 10^{-3}$	1.08
2	0.11	0.2	1:1.1	$5.54M$ HCl	1.16	$0.85 \cdot 10^{-3}$	0.80
3	0.2	0.2	1:1.1	0	1.27	$0.37 \cdot 10^{-3}$	0.80
4	0.2	0.02	1:1.1	0	1.44	$0.13 \cdot 10^{-3}$	0.36
5	0.02	0.02	3:1	$5M$ HCl	1.89	$0.05 \cdot 10^{-3}$	–
6	0.2	0.2	2:1	0	2.01	$0.10 \cdot 10^{-3}$	0.16
7	0.02	0.02	3:1	0	2.98	10^{-6}	0

Table 1 gives the synthesis conditions and some properties of zirconyl phosphate samples. The exchange capacity was determined from titration curves with

Figure 2

Figure 2: Figure 2

sodium alkali. The electrical conductivity was found from the point equal to the electrical conductivity of the ion exchanger and of the solution in equilibrium with it, using direct current ([11]).

Table 2

Ion	pH	Γ_M, meq/g	Ion	pH	Γ_M, meq/g
Na^{++}	2.5	0.3	Ba^{++}	2.0	4.50
Mg^{++}	2.1	1.24*	Zn^{++}	2.0	4.68
Ca^{++}	2.0	4.30	Cu^{++}	1.8	5.84

* $M_{Mg^{++}} = 0.2$.

From the data in Table 1 it is evident how the concentration of the reagents, the acidity of the solution, and the molar ratio of the initial components affect the composition of the precipitate: the value of K increases with decreasing acidity of the solution and with increasing ZrO_2/P_2O_5 ratio in the initial solutions. Precipitates with $K \approx 1$ are obtained if precipitation is carried out under conditions of an excess of phosphoric acid and high acidity of the zirconium salt solution (which leads to a decrease in the degree of hydrolysis of the salt).

Using titration curves, the exchange capacity of the zirconyl phosphate samples was determined, represented as a function of pH and of the value of K in Fig. 1. Fig. 1 shows that the exchange capacity for all zirconyl phosphate samples depends on pH, and for each pH value the exchange capacity decreases as the value of K increases. Since the capacity recalculated per 1 mole of P_2O_5 in the sample also decreases with increasing K, it may be assumed that as the molar ratio increases, not only does the number of ionogenic groups decrease, but their ability to dissociate is also lowered. The electrical conductivity of the samples changes sympathetically with the composition: the greater the value of K, the lower its electrical conductivity. For sample No. 1 (Table 1), a static-method study was carried out of the absorption capacity for monovalent ions (Na^+, Li^+) and divalent (Ca^{++}, Mg^{++}, Ba^{++}, Cu^{++}, Zn^{++}) cations as a function of the concentration and pH of the equilibrium solution. Results for the absorption of calcium and sodium at various concentrations and pH are presented in Fig. 2, which shows that divalent calcium is absorbed in acidic and neutral media considerably more strongly than the monovalent sodium ion. The absorbed amount of sodium ions Γ_{Na^+} in the acidic region is signifi-

Fig. 2. Curves of absorption of Ca^{++} ions (*a*) and Na^+ ions (*b*) on sample 1 of zirconyl phosphate for different concentrations of the metal ion in solution (1—0.02 M; 2—0.2 M; 3—0.5 M; 4—1.0 M).

Fig. 3. Dependence of the e.m.f. on the logarithm of the mean activity of sodium chloride or hydrochloric acid in the external solution.

Figure 3: Fig. 3. Dependence of the e.m.f. on the logarithm of the mean activity of sodium chloride or hydrochloric acid in the external solution.

markedly less than calcium ions, but in the neutral region Γ_{Na^+} approaches the limiting value (6-7 meq/g). Calcium ions, even in an acidic medium, displace from the precipitate the second hydrogen ion of phosphoric acid, as a result of which a considerable part of the exchange capacity is exhausted already in an acidic medium. It is of interest to compare the absorption values of several divalent ions and sodium ions at low pH and at a cation concentration equal to $0.5\,M$ (Table 2).

Fig. 3. Dependence of the e.m.f. on the logarithm of the mean activity of sodium chloride or hydrochloric acid in the external solution. 1 —electrodes from a sample with $K = 1.07$ in HCl solutions, 2 —the same in NaCl solutions, 3 —electrodes from a sample with $K = 1.89$ in HCl solutions, 4 —electrodes from a sample with $K = 3.25$ in HCl solutions.

If the cations studied are arranged successively in decreasing strength of affinity for zirconyl phosphate ($K = 1$), the following series is obtained:

$$\mathrm{Cu}^{++} > \mathrm{Zn}^{++} > \mathrm{Ba}^{++} > \mathrm{Ca}^{++} > \mathrm{Mg}^{++} > \mathrm{Na}^{+} > \mathrm{Li}^{+}.$$

The high selectivity of zirconyl phosphate toward copper ions is noteworthy.

At present, ion-exchange materials are widely used for preparing membranes employed in fuel cells, in electrodialysis processes, and also for manufacturing membrane electrodes. In the present work, the electrode behavior of membranes made from zirconyl phosphates of different composition was investigated. To prepare the electrodes, by the method already described [12], heterogeneous membranes were used, obtained from fine powders of zirconyl-phosphate ion exchangers and an inert binder (polymethyl methacrylate, polystyrene) by pressing or by the casting method [12].

For studying membrane potentials, the following galvanic cell was used:

$$\mathrm{Ag}\,|\,\mathrm{AgCl},\ \mathrm{HCl}\,|\,\mathrm{membrane}\,|\,\mathrm{HCl},\ (\mathrm{NaCl}),\ \mathrm{AgCl}\,|\,\mathrm{Ag}.$$

$$m' = \mathrm{const} \qquad m''$$

The dependence of the e.m.f. of this cell on the logarithm of the mean activity of HCl or NaCl is shown in Fig. 3, from which it is seen that membrane electrodes prepared from a sample with K close to unity exhibit the theoretical hydrogen and sodium functions (straight lines 1 and 2 have a slope coefficient $2\vartheta^* = 118$ mV at 25° ($\vartheta = 2.3RT/F$)). Electrodes obtained from zirconyl-phosphate samples with $K \gg 1$ give deviations from the hydrogen function (the slope coefficient of straight lines 3 and 4 $< 2\vartheta$), the magnitude of which increases with increasing K. This fact is probably connected with indications in the literature that zirconyl-phosphate exchangers with $K > 1$ are capable of absorbing anions from acidic solutions.

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Note: Figure translations are in progress. See original paper for figures.

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