Physical Chemistry

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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Spectrophotometric Study of Chloride Solutions of Zirconium in Connection with Its Adsorption on Fluoroplastic-4

Earlier we showed that the distribution coefficient of zirconium-95 between solution and the nonionogenic surface of fluoroplastic-4 decreases with increasing HCl concentration and depends on the nature of the cations of chlorides of the first group. At constant ionic strength, the adsorption of zirconium-95 increased in the series (Fig. 1):

$$\mathrm{Li}^+ \ll \mathrm{H}^+ \ll \mathrm{Na}^+ < \mathrm{K}^+ < \mathrm{NH}_4^+.$$

The decrease in adsorption of zirconium-95 with increasing HCl concentration was explained by a decrease in the degree of hydrolysis of zirconium and by an increase in the fraction of chloride ions in neutral complexes of the type $[\mathrm{Zr(OH)}_x\mathrm{Cl}_{4-x}]$, which were adsorbed on fluoroplastic-4. It was natural to suppose that the influence of the nature of the cations on the magnitude of adsorption is also due to differences in the degree of hydrolysis and complex formation of zirconium with chloride ions in solutions of the corresponding chlorides. It is known that the active concentration of HCl increases in the series KCl $<$ NaCl $>$ LiCl, and, consequently, the degree of hydrolysis of zirconium in this direction should decrease. To clarify the influence of the nature of cations on the complex formation of Zr with Cl^- ions, we used the spectrophotometric method.

Fig. 1. Dependence of the adsorption of zirconium-95 on fluoroplastic-4 from 1 *N* HCl on the concentration of chlorides of the first group. 1 $-\mathrm{NH_4Cl}$, 2 $-$KCl, 3 $-$NaCl, 4 $-$HCl, 5 $-$LiCl.
$K = \Gamma/C$, where Γ is g-at. Zr per 1 cm^2, C is g-at. Zr per 1 ml.

Measurements were carried out on an SF-4 spectrophotometer. All reagents were carefully recrystallized or redistilled. Spectrally pure zirconium oxychloride was used for preparing the solutions. The data given below correspond to equilibrium solutions and are expressed as optical density or as the molar extinction coefficient.

As can be seen from Fig. 2, in 2 N hydrochloric acid, where zirconium is present mainly in the form of ZrO^{2+} or Zr^{4+} ions, absorption is very small. In hydrochloric acid the optical density of zirconium solutions increases owing to the formation of complexes $ZrCl_x^{(4-x)+}$. In 8 N and 9 N HCl, a maximum appears in the absorption spectrum in the region 220–225 mμ, probably corresponding to the formation of the complexes $ZrCl_5^-$ and $ZrCl_6^{2-}$.

Thus, the integral magnitude of the optical density of chloride solutions of zirconium in the region 213–250 mμ characterizes the degree of complexation of zirconium with chloride ions.

In Figs. 3 and 3a are shown the absorption spectra of zirconium in solutions of chlorides of the first group. The differences in the spectra are especially noticeable in the short-wavelength region and show that the intensity of complex formation decreases in the series:

$$H^+ > Li^+ > Na^+ > K^+ > NH_4^+.$$

Table 1

Optical density of zirconium chloride solutions in the presence of cations of the first group
(zirconium concentration $2 \cdot 10^{-2}$ M)

Solution composition	$D \cdot 10^3$ at $\lambda = 214$ mμ	Solution composition	$D \cdot 10^3$ at $\lambda = 214$ mμ
$\mu = 2.2$		$\mu = 3.0$	
$2\,N$ HCl	192	$3.0\,N$ HCl	525
$0.2\,N$ HCl + $2.0\,N$ LiCl	113	$1.0\,N$ HCl + $2.0\,N$ LiCl	180
$0.2\,N$ HCl + $2.0\,N$ NaCl	62	$1.0\,N$ HCl + $2.0\,N$ NaCl	125
$0.2\,N$ HCl + $2.0\,N$ KCl	54	$1.0\,N$ HCl + $2.0\,N$ KCl	114
$0.2\,N$ HCl + $2.0\,N$ NH_4Cl	44	$1.0\,N$ HCl + $2.0\,N$ NH_4Cl	98

Table 1 gives the values of the optical density of more concentrated zirconium solutions. The cation series is preserved. Consequently, the intensity of complex formation of zirconium with chloride ions depends on the nature of the cations of neutral salts.

Fig. 2. Absorption spectra of zirconium solutions ($2 \cdot 10^{-3}$ M) in hydrochloric and perchloric acid. I—9 N HCl, II—8 N HCl, III—6 N HCl, IV—2 N HCl, V —1 N HCl, VI—2 N $HClO_4$. D—optical density; ε—molar extinction coefficient.

Figure 2: Fig. 2. Absorption spectra of zirconium solutions ($2 \cdot 10^{-3}$ M) in hydrochloric and perchloric acid. I—9 N HCl, II—8 N HCl, III—6 N HCl, IV—2 N HCl, V—1 N HCl, VI—2 N $HClO_4$. D—optical density; ε—molar extinction coefficient.

Figure 3

Figure 3: Figure 3

The optical densities of solutions of Zr in NaCl, KCl, and NH_4Cl are very close to one another. A distinct dependence of the magnitude of zirconium adsorption on its state is manifested in this case for two groups of solutions: NaCl, KCl, NH_4Cl, on the one hand, and HCl, LiCl, on the other. With increasing concentration of NaCl, KCl, and NH_4Cl, the adsorption of zirconium (Fig. 1), in comparison with its adsorption from pure acid, increases, whereas the addition of HCl and LiCl decreases the adsorption. Apparently, in NaCl, KCl, and NH_4Cl solutions the formation of zirconium complexes with chloride ions occurs mainly at the expense of free valences, without displacement of hydroxyl groups from the inner sphere of the complexes. This leads to an increase in the fraction of neutral zirconium forms in solution while preserving their adsorptive capacity. The adsorption of zirconium increases (the "salting-out" effect).

Fig. 2. Absorption spectra of zirconium solutions ($2 \cdot 10^{-3}$ M) in hydrochloric and perchloric acid. I—9 N HCl, II—8 N HCl, III—6 N HCl, IV—2 N HCl, V —1 N HCl, VI—2 N $HClO_4$. D—optical density; ε—molar extinction coefficient.

With increasing concentration of HCl and LiCl, the complex formation of zirconium is probably accompanied by a considerable decrease in the degree of its hydrolysis and by a decrease in the adsorptive capacity of the neutral complexes formed.

At equal chloride-ion concentration in NaCl, KCl, and NH_4Cl solutions, the magnitude of zirconium adsorption is significantly higher than in HCl solutions and

LiCl. This agrees with the spectrophotometric data, which show that in the presence of Na^+, K^+, and NH_4^+ the degree of complexation of zirconium with

Fig. 3. Absorption spectra of chloride solutions of zirconium ($2 \cdot 10^{-3}$ M, $\mu = 2$).
I —2 N HCl; II —0.2 N HCl + 1.8 N LiCl; III —0.2 N HCl + 1.8 N NaCl; IV —0.2 N HCl + 1.8 N KCl; V —0.2 N HCl + 1.8 N NH_4Cl. D —optical density; ε —molar extinction coefficient. (In Fig. 3 on the right, part of the spectra is presented on an enlarged scale.)

chloride ions is considerably lower than in solutions containing H^+ and Li^+ ions.

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