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DEPENDENCE OF THE ABSORPTION SPECTRA OF SOLUTIONS AND ISOMORPHOUS ALUM CRYSTALS ON CHROMIUM CONTENT

![Fig. 1](image)

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

PHYSICAL CHEMISTRY

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DEPENDENCE OF THE ABSORPTION SPECTRA OF SOLUTIONS AND ISOMORPHOUS ALUM CRYSTALS ON CHROMIUM CONTENT

(Presented by Academician A. V. Shubnikov on 18 VII 1956)

In theoretical works devoted to the study of the question of the absorption of light by impurities in dielectrics (1–3), only those cases are considered in which the "absorption centers" are independent of one another. However, it is known that Beer' s law, which reflects this assumption, is not always fulfilled. In those cases where deviations from it cannot be explained chemically, the cause should apparently be sought in the interaction of the absorption centers. It is of interest to determine under what conditions this interaction becomes so significant that it is reflected in the absorption spectra.

Fig. 1. Dependence of the position of the maxima of the absorption bands in alum crystals on chromium content.
$a - \nu_{\text{max}} = 24600\ \text{cm}^{-1}$,
$b - \nu_{\text{max}} = 17700\ \text{cm}^{-2}$

The absorption spectra of mixed crystals and solutions of aluminum potassium and chromium potassium alums were investigated; in them chromium ions isomorphously replace Al^{3+} ions and constitute the coloring impurity. An analogous, but less complete, investigation had earlier been carried out by Ritschl and Müller (4) on corundum crystals Al_2O_3 colored by an isomorphous impurity of Cr^{3+}. It was of interest to follow the behavior of broad bands in the spectra of crystals of different structure as a function of the concentration of one and the same coloring impurity.

The absorption spectra of alum crystals and solutions were measured in the wavelength range 250–700 mμ at room temperature. In the visible part of the spectrum the measurements were carried out on a UM-2 monochromator by the photoelectric method; in the ultraviolet region, on a Q-12 spectrograph. The range of chromium concentration variation in the crystals was from 2.9 to 100

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Fig. 2. Fulfillment of Beer' s law for mixed alum crystals. a $-\nu$max = 17700 cm^{-1}, b $-\nu$max = 24600 cm^{-1}

Figure 2: Fig. 2. Fulfillment of Beer' s law for mixed alum crystals. a $-\nu$max = 17700 cm^{-1}, b $-\nu$max = 24600 cm^{-1}

mole %; in solutions, $7 \cdot 10^{-3}$-$5.6 \cdot 10^{-1}$ mole %.

In the absorption spectra of alum crystals there are three broad absorption bands, $\nu_{\text{max}} = 17700$, 24600, and 38750 cm^{-1}, the last of which lies very close to the edge of the fundamental absorption, and therefore it could not be studied in detail. The position of the maxima of the absorption bands of the other two bands and their half-width do not depend on the chromium concentration (Fig. 1). The areas bounded by the spectral-absorption curve and the frequency axis are proportional to the chromium concentration, as are the absorption coefficients at the maxima. Beer' s law is strictly fulfilled (Fig. 2). The shape of the bands is close to the shape of the Gaussian error curve. The oscillator strengths are: $f_{17700} = 2.25 \cdot 10^{-5}$ and $f_{24600} = 2.16 \cdot 10^{-5}$.

Investigation of the positions of the maxima of the corresponding broad absorption bands in the spectra of corundums colored with chromium showed that

the bands shift in the spectrum toward lower frequencies as the chromium concentration increases, with a strong shift observed in the concentration interval 8.4-100 mol.%, while for lower concentrations the positions of the bands are almost constant. According to Tilo [5], the magnetic and thermochemical properties of these crystals, as well as the lattice parameters, specific weight, and luminescence yield, undergo analogous changes when the chromium concentration is varied. Tilo and Sauer [6] investigated the dependence of color, lattice constant, density, and thermochemical properties on chromium concentration for mixed spinel crystals $\text{MgO} \cdot \text{Al}_2\text{O}_3 - \text{MgO} \cdot \text{Cr}_2\text{O}_3$. The curves of the dependence of the properties of corundums and spinels on chromium concentration

Fig. 2. Fulfillment of Beer' s law for mixed alum crystals.
a $-\nu_{\text{max}} = 17700$ cm^{-1}, **b** $-\nu_{\text{max}} = 24600$ cm^{-1}

proved to be similar, but the limiting concentration for the spinel is 15 mol.%. Tilo explains the phenomena described by the fact that there are two types of bonding of chromium ions in these crystals: at low concentrations, when they exist independently of one another, and at high concentrations, when each ion has at least one identical ion as its nearest neighbor. A rough calculation shows that such a limiting concentration for corundums is 8.4 mol.%, and for spinels 15 mol.%. The chromium ions in mixed alum crystals behave independently of concentration. The reason for this difference is the difference in the structure of the crystals under consideration. In corundum the chromium ion is located at the center of an octahedron; in spinels, at the center of a tetrahedron of oxygen ions, with the shortest distance in corundums between metal ions being $\simeq 2$ Å. In alum crystals the chromium ion is located at the center of an octahedron of

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H_2O molecules situated at a distance of 1.98 Å from it.

Chromium belongs to the transition elements. The electronic transitions corresponding to the broad absorption bands in the spectra of the crystals considered evidently take place within the unfilled $3d$-shell, since the oscillator strength is small—of the order of 10^{-4}–10^{-5}. During absorption of light, a redistribution of electrons occurs within the $3d$-shell; consequently, the electric field created by the ion changes little at large distances from it, and strong interaction can occur only with the nearest neighbors. As shown above, the distance to them must be of the order of 2 Å. The chromium ions in alum crystals are shielded by an aqueous shell of six water molecules; therefore, a change in the chromium concentration is not reflected in the absorption spectra.

This assumption is confirmed by studies of the absorption spectra of solutions of mixed alums. It is known that when alums dissolve, the chromium ion passes into solution in the form of the complex $[Cr(H_2O)_6]^{3+}$, retaining its aqueous shell. The absorption spectra of the solutions are very close to the spectra of the crystals; the half-widths of the corresponding bands are almost equal, and the bands in the spectra of the solutions are shifted somewhat toward lower frequencies. Beer' s law is strictly fulfilled (Fig. 3). The positions of the band maxima and their half-width do not depend on the chromium concentration. The shape of the bands

is close to the form of a Gaussian error curve. The oscillator strengths are equal to: $f_{17300} = 6.2 \cdot 10^{-5}$ and $f_{24300} = 4.0 \cdot 10^{-5}$.

Consequently, a change in the more distant neighbors of chromium has little effect on the absorption spectra of chromium ions. The principal role is played by the immediate environment, the replacement of which leads to significant changes in the spectrum. As shown by a study of the absorption of solutions of the green modification of alums—the basic chromium complexes and the complexes $[Cr(SO_4)_3]^{3-}$—a larger shift of the bands in the spectrum is observed, as well as a significant change in the half-width of the bands (up to 13%) in going from alum solutions to these solutions than in going to crystals.

Fig. 3. Fulfillment of Beer' s law for mixed alum solutions.
a–$\nu_{\max} = 17300$ cm^{-1}, b–$\nu_{\max} = 24300$ cm^{-1}.

The described features in the behavior of broad bands in the spectra of solutions and crystals of mixed alums show that, as the "absorption centers" considered in the theory of A. S. Davydov and S. I. Pekar, in the present case one should regard not chromium ions, but complexes of the chromium ion, $[Cr(H_2O)_6]^{3+}$.

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