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Academician I. V. TANANAEV and B. F. DZHURINSKII

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Figure 1. Absorption spectra of melts in the systems CsCl—$CoCl_2$ (a), RbCl—$CoCl_2$ (b). The numbers correspond to the following molar ratios MCl/$CoCl_2$: a: 1 –0, 2 –0.9, 3 –1, 4 –2, 5 –326; b: 1 –1, 2 –2, 3 –47

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Abstract

Full Text

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APPLICATION OF SPECTROPHOTOMETRY TO THE STUDY OF THE COMPOSITION AND STRUCTURE OF COBALT CHLORIDE COMPLEXES

The crystal-field bands in the absorption spectrum of complex ions are directly connected with the structure of the ligand field. This circumstance has made it possible, on the basis of spectrophotometric measurements, to obtain considerable information concerning the composition, stability, and structure of complex particles in liquid media. In contrast to liquid media, the connection between the composition and structure of crystalline substances is not direct. However, the application of spectrophotometry in physicochemical analysis can in this case also provide an indication of the composition and structure of complex compounds. The absorption spectra of anhydrous $CoCl_2$ and of complexes containing the ion $[CoCl_4]^{2-}$ have been studied repeatedly (1−6). Taking into account X-ray structural data makes it possible to conclude (4−6) that the absorption band with maxima at 530 and 580 mμ belongs to the octahedral ion $[CoCl_6]^{4-}$, while the band with maxima at 412, 450, 535, 625, 660, and 685 mμ is associated with the existence of tetrahedral ions $[CoCl_4]^{2-}$.

Fig. 1. Absorption spectra of melts in the systems CsCl—$CoCl_2$ (*a*), RbCl—$CoCl_2$ (*b*). The numbers correspond to the following molar ratios MCl/$CoCl_2$: *a*: 1 –0, 2 –0.9, 3 –1, 4 –2, 5 –326; *b*: 1 –1, 2 –2, 3 –47.

We obtained absorption spectra of crystalline melts in systems composed of anhydrous $CoCl_2$ and alkali-metal chlorides.

The substance or mixture of substances in the molten state was applied in a thin layer to the walls of a closed quartz test tube, and the absorption of the

Figure 2

Figure 2: Figure 2

thin polycrystalline film obtained in this way was measured on

spectrophotometer SF-4. The experimental data are presented in Figs. 1-4.

Figure 1 presents the absorption spectra of melts in the systems $CoCl_2$—CsCl (a) and $CoCl_2$—RbCl (b). Curve 1a represents the visible region of the absorption band of $CoCl_2$, which has an octahedral structure. The band has maxima at 535 and 590 mμ. The absorption of a $CoCl_2$ melt with CsCl at a molar ratio of 1 : 1 is represented by curve 3a. As can be seen, the curve retains the character of the octahedral band, but acquires a right-hand shoulder. It was assumed that this is connected with insufficient accuracy of the stoichiometry of the composition, which gives rise to traces of strongly absorbing tetrahedral complexes. Indeed, a melt with the molar ratio

Fig. 2. Absorption spectrum of melts in the systems KCl—$CoCl_2$ (a), NaCl—$CoCl_2$ (b). The numbers correspond to the following molar ratios MCl/$CoCl_2$.
a: 1 –1, 2 –1.8, 3 –2, 4 –900;
b: 1 –1, 2 –2, 3 –4, 4 –5, 5 –105

of CsCl to $CoCl_2$ equal to 0.9 has no right-hand shoulder in the absorption pattern (curve 2a). Thus, on fusion of CsCl with $CoCl_2$ in the ratio 1 : 1, an octahedral complex of composition $CsCoCl_3$ is probably formed. This compound is blue in color, solidifies as needles, and does not hydrate in air.

Curve 4a represents the absorption spectrum of a CsCl melt with $CoCl_2$ in the ratio 2 : 1. The absorption spectrum fully corresponds to the absorption pattern characteristic of a tetrahedral complex of composition Cs_2CoCl_4 ([4]–[6]). The compound obtained is stable in air for an arbitrarily long time. Melts of CsCl with $CoCl_2$ containing larger molar fractions of CsCl retain the spectral structure characteristic of tetrahedral complexes (as illustrated by curve 5a for a melt with ratio 326). The RbCl—$CoCl_2$ system is analogous to the one just considered. It should merely be noted that the absorption band of the RbCl melt with $CoCl_2$ in the ratio 1 : 1 has no tetrahedral right-hand shoulder. The needle-shaped blue crystals of $RbCoCl_3$ are stable in air for a long time; however, with time they nevertheless undergo hydration, passing into a pink hydrate form.

Fusibility in the KCl—$CoCl_2$ system was studied by M. S. Golubeva and A. G. Bergman ([7]). Two congruently melting compounds, $CoCl_2 \cdot 2KCl$ and $5CoCl_2 \cdot 9KCl$, and one incongruently melting compound, $CoCl_2 \cdot KCl$, were found. The spectrophotometric measurements are in agreement with these data, Fig. 2a. Curve 1a relates to the melt $CoCl_2 \cdot KCl$. As can be seen, it combines features of the spectra of octahedral and tetrahedral complexes, with a quantitative predominance of octahedral ones.

Curves 2 and 3 (Fig. 2a) represent the absorption spectra of the compounds

Fig. 3 and Fig. 4: absorption spectra plots

Figure 3: Fig. 3 and Fig. 4: absorption spectra plots

$5CoCl_2 \cdot 9KCl$ and $CoCl_2 \cdot 2KCl$, respectively. Increasing the molar fraction of KCl in its melts with $CoCl_2$ does not lead to the appearance of new structures (illustrated by curve 4a for a melt with a molar ratio of 940). Tetrahedral complexes are stable in air indefinitely.

According to thermal-analysis and crystal-optical measurements ([8]), in the NaCl—$CoCl_2$ system below the eutectic point one compound of composition $2NaCl \cdot CoCl_2$ is formed. The absorption spectrum of a melt of composition $NaCl \cdot CoCl_2$ indicates the formation of a tetrahedral complex (Fig. 2b, curve 1). In a melt of composition $2NaCl \cdot CoCl_2$, two phases are visually observed: a tetrahedral phase

Fig. 3. Absorption spectra of melts in the LiCl—$CoCl_2$ system. The numbers correspond to the following molar ratios LiCl/$CoCl_2$:
1 –0.085, 2 –2, 3 –200

Fig. 4. Differential absorption curves of 0.00248 M solutions of $Co(NO_3)_2$ in nitrate melt containing various amounts of KCl. Curves $1, 2, 3$ refer to the following pairs of molar concentrations of KCl, respectively: 0.139 and 0.000, 0.282 and 0.139, 1.635 and 0.282

and a weakly absorbing octahedral phase. The absorption spectrum of the tetrahedral phase is shown by curve 2 (Fig. 2b). Melts with a higher NaCl content continue to retain both of the indicated phases. At the same time, the fraction of the octahedral phase increases. For melts of composition $4NaCl \cdot CoCl_2$ and $5NaCl \cdot CoCl_2$, we succeeded in separating these phases. The corresponding absorption spectra are represented by curves 3 and 4 (Fig. 2b). A melt with a ratio of NaCl to $CoCl_2$ of 105 contains only the octahedral dendritic phase, curve 5 (Fig. 2b). Evidently, it is a limited solid substitution solution of $CoCl_2$ in NaCl. In this case the character of coordination of the Co^{2+} ion is retained.

Melts of $CoCl_2$ with LiCl are homogeneous over the entire range of component ratios, both in appearance and in optical properties. In view of the closeness of the ionic radii of Co^{2+} (0.82) and Li^+ (0.78), their mutual and continuous substitutions in the crystal lattices of $CoCl_2$ and LiCl are possible, with preservation of the octahedral cubic crystal field for the Co^{2+} ion. It is seen from Fig. 3 that the absorption spectra of melts in the LiCl—$CoCl_2$ system retain the features characteristic of octahedral complexes over a wide range of component ratios. The optical data are in agreement with the results of studying fusibility in the same system ([9]) and contradict the results of Ferrari and Baroni ([10]) (the fusibility curve has two minima and a maximum corresponding to the compound Li_2CoCl_4).

Thus, the cobalt ion in chloride complex compounds may be found both in octahedra and in tetrahedra, showing a preference for tetrahedra. The tendency to enter octahedra decreases in the series Cs—Li for complex compounds with an alkali-metal atom in the outer sphere. At the same time, the closeness of the ionic radii of Co^{2+}, Na^{+}, and Li^{+} creates conditions for the entry of Co^{2+} into the NaCl and especially LiCl lattices with preservation of octahedral coordination. The tendency toward the formation of higher complexes decreases in the series Cs—Li.

In an octahedral crystal field the ground ^4F level of the Co^{2+} ion splits into three sublevels Γ_4, Γ_5, and Γ_2. The next level, which is not split in an octahedral field, is ^4P. Accordingly, the bands corresponding to the transitions $^4F(\Gamma_4) \to {}^4F(\Gamma_5)$ and $^4F(\Gamma_4) \to {}^4F(\Gamma_2)$, at small splittings, should lie in the infrared region. The band of the $^4F(\Gamma_4) \to {}^4P(\Gamma_4)$ transition in a weak crystal field should lie in the visible region. Indeed, the center of gravity of the principal band in the visible region for $CoCl_2$ and $MeCoCl_3$ compounds lies at 590 and 600 mμ. Taking for the F—P transition

$$\gamma = 3.5(E_1 - E_2) + 15400$$

(11), where $E_1 - E_2$ is the splitting of the F level and 15400 cm^{-1} is the distance between the F and P levels in the free Co^{2+} ion, we find $E_1 - E_2 = \sim 3300$ cm^{-1} for $CoCl_2$ and 2200 cm^{-1} for $MeCoCl_3$. As can be seen, if the displacement of the P level in the crystal field is disregarded, introduction of an alkali metal into the outer sphere of the complex sharply reduces the strength of the crystal field and, consequently, leads to a decrease in the already weak excess of the stabilizing force of the octahedral field over the tetrahedral one (12). It is characteristic that the replacement of Na^{+} and Li^{+} ions by Co^{2+} ions in alkali chlorides is not associated with a displacement of the octahedral band characteristic of $CoCl_2$, even in the case of solid solutions with LiCl.

The fact that the cobalt ion prefers a tetrahedral sphere is reflected in the chemistry of solutions. According to data from the preceding work (13), differential curves of the absorption spectra of two $Co(NO_3)_2$ solutions in a nitrate melt containing different amounts of KCl were constructed. In our opinion, the resulting picture characterizes the absorption bands of those complexes which are present in the concentration interval of addends under study in larger amounts. Curve 3 in Fig. 4 is analogous to the curves that we obtained for tetrahedral crystalline complexes. As can be seen, the absorption maxima of the lower complexes belong, approximately, to 620 and 660 mμ. Earlier (13) we already suggested that these bands correspond to the complex particles $[CoCl_2]$ and $[CoCl_3]^-$. Taking into account that the absorption maximum of the higher nitrate complex belongs to 550 mμ (13), while the maximum of the octahedral $[CoCl_6]^{4-}$ ion is found at about 590 mμ, the complexes $[CoCl_2]$ and $[CoCl_3]^-$ should probably be assigned a tetrahedral structure and the composition $[CoCl_2(NO_3)_2]^{2-}$ and $[CoCl_3NO_3]^{2-}$.

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