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Figure 1

Figure 1: Figure 1

Abstract

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STUDY OF THE INTERACTION IN THE SYSTEMS $Co(NO_3)_2$–KBr, $Co(NO_3)_2$–KI IN A NITRATE MELT

Previously we studied the interaction in the system $Co(NO_3)_2$–KCl in a nitrate melt (^{1}). The present work is devoted to the investigation of the interaction in the systems $Co(NO_3)_2$–KBr, $Co(NO_3)_2$–KI in a nitrate melt and under direct contact of the components.

The method of high-temperature spectrophotometry has already been described by us (^{1}). As solvent we used a molten mixture,

Fig. 1. Changes in the absorption spectrum of a 0.0025 *M* solution of $Co(NO_3)_2$ associated with the formation of bromide complexes at 160° (*a*) and 200° (*b*). The numbers correspond to the following ratios

$$\frac{C_{\mathrm{KBr}}}{C_{\mathrm{Co(NO_3)_2}}}: \quad 1—0, \quad 2—8, \quad 3—16, \quad 4—32, \quad 5—64, \quad 6—128, \quad 7—256, \quad 8—400,$$

8^a–saturated solution

containing 45 mol.% $LiNO_3$ and 55 mol.% KNO_3. Since KBr and, especially, KI are unstable in an acidic nitrate melt, while $Co(NO_3)_2$ is unstable in an alkaline nitrate melt, measures were taken to maintain the appropriate acidity of the melt. This was achieved by preliminary single melting and freezing for the system with KBr, and fourfold melting and freezing for the system with KI, of an acidic solution of $Co(NO_3)_2$ in the nitrate melt; for each experiment a fresh portion of the $Co(NO_3)_2$ solution treated in this way was taken.

Figure 1 presents changes in the absorption spectrum of a 0.0025 *M* solution of $Co(NO_3)_2$ associated with the formation of bromide complexes. With increasing KBr concentration, the following appear successively: a hidden maximum at 580

Fig. 2. Isomolar series in the system $Co(NO_3)_2$—K_2Br_2

Figure 2: Fig. 2. Isomolar series in the system $Co(NO_3)_2$—K_2Br_2

mμ, maxima at 610, 640, 660, and 695 mμ, and a hidden maximum at about 730 mμ. The independence of their appearance, especially evid—

···when comparing data relating to different temperatures, makes it possible to assign the observed maxima to the following individual complex ions: $[CoBr]^+$, $[CoBr_2]$, $[CoBr_3]^-$, $[CoBr_4]^{2-}$, $[CoBr_5]^{3-}$, $[CoBr_6]^{4-}$. S. A. Shukarev and O. A. Lobanova (^{2}), in a spectrophotometric study of acetone solutions of cobalt bromide complexes, found absorption maxima at 720, 700, 670, 640, and 580 mμ, which they attributed to the formation of the following complex compounds, respectively: $Li_4[CoBr_6]$, $Li_2[CoBr_4 \cdot 2\,\text{acet.}]$, $Li[CoBr_3 \cdot 3\,\text{acet.}]$, $[CoBr_2 \cdot 4\,\text{acet.}]$,

Fig. 2. Isomolar series in the system $Co(NO_3)_2$—K_2Br_2 at a total concentration of 0.025 M/l.

$$n = \frac{C_{K_2Br_2}}{C_{Co(NO_3)_2}}.$$

1—160°, 2—200°; *a*—610, *b*—680, *c*—660, *d*—700 mμ

$[CoBr \cdot 5\,\text{acet.}]Br$. They declare the complex compound of composition $Li_3[CoBr_5 \cdot \text{acet.}]$ to be disproportionating. Meanwhile, the values found by Lobanova (^{3}) for the successive stability constants, $K_4 = 21$, $K_5 = 8$, $K_6 = 2$, contradict the idea of disproportionation of this complex. It should also be said that the curves on the basis of which the individual absorption maxima were isolated (^{2,3}) clearly indicate the existence of a principal maximum at 700 mμ for $\bar{n} = 5$ and at 670 mμ for $\bar{n} = 4$. From the curve for $\bar{n} = 2$, nothing definite can be said at all.

Thus, the positions of the main absorption bands found by us and by the authors cited basically coincide and can be assigned to the corresponding complexes. The successive shift of the absorption bands into the long-wavelength region with increasing content of Br^- ions in the complex up to the complex of composition $[CoBr_6]^{4-}$ indicates a successive weakening of the crystal field surrounding the Co^{2+} ion, while the octahedral configuration is essentially preserved. The presumed positions of the absorption bands of the individual complexes were calculated on the basis of the concept of averaging the influence of the crystal field of the ligands when, in the octahedral complex $[Co(NO_3)_6]^{-4}$, NO_3^- ions are replaced by Br^- ions. It turned out that complexes of the compositions $[Co(NO_3)Br_5]^{4-}$, $[Co(NO_3)_2Br_4]^{4-}$, $[Co(NO_3)_3Br_3]^{4-}$, $[Co(NO_3)_4Br_2]^{4-}$, and $[Co(NO_3)_5Br]^{4-}$ should absorb in the wavelength region 695, 658, 604, and 580 mμ. The good agreement between the calculated and experimental positions of the absorption maxima indicates the existence of the observed individual complex ions.

Fig. 3

Figure 3: Fig. 3

Figure 2 presents the data of the isomolar series in the system $Co(NO_3)_2$—K_2Br_2 at a total concentration of 0.025 M. As can be seen, complexes are formed in the system that tend toward the composition $[CoBr_2]$ at $\lambda = 610$ mμ and a temperature of 200°, and toward higher coordination numbers (with respect to Br^-) at greater wavelengths and 160°.

Figure 3 presents the changes in the absorption spectrum of a 0.0025 M solution of $Co(NO_3)_2$ in a nitrate melt, associated with the formation of iodide complexes. As the concentration of KJ is increased, the following appear successively: a hidden maximum near 590 $m\mu$, maxima at 610, 650, 695, 750, and 780 $m\mu$, which may be assigned, respectively, to the complex ions $[Co(NO_3)_5J]^{4-}$, $[Co(NO_3)_4J_2]^{4-}$, $[Co(NO_3)_3J_3]^{4-}$, $[Co(NO_3)_2J_4]^{4-}$, $[Co(NO_3)J_5]^{4-}$, and $[CoJ_6]^{4-}$. On the basis of the positions of the absorption bands of the octahedral ions $[Co(NO_3)_6]^{4-}$ (555 $m\mu$) and $[CoJ_6]^{4-}$ (780 $m\mu$), the positions of the bands of the intermediate complexes were calculated under the assumption that the octahedral configuration is retained and that the influence of the ligand crystal fields is averaged. The calculated absorption bands for the ions $[Co(NO_3)_5 \cdot J]^{4-}$, $[Co(NO_3)_4J_2]^{4-}$, $[Co(NO_3)_3J_3]^{4-}$, $[Co(NO_3)_2J_4]^{4-}$, $[Co(NO_3)J_5]^{4-}$ lie in the wavelength region, respectively, 585, 615, 650, 695, and 730 $m\mu$. As can be seen, with the exception, apparently, of the tetrahedrally distorted $[Co(NO_3)J_5]^{4-}$, the calculated bands coincide with the observed ones, which confirms the existence of octahedral mixed iodide complexes of Co^{2+}.

Fig. 3. Changes in the absorption spectrum of a 0.0025 M solution of $Co(NO_3)_2$ associated with the formation of chloride complexes at 160°. The numbers correspond to the following ratios:

$$\frac{C_{\mathrm{KJ}}}{C_{\mathrm{Co(NO_3)_2}}}: \quad 1—0, \quad 2—32, \quad 3—48, \quad 4—64, \quad 5—80, \quad 6—96, \quad 7—128,$$

1^a –absorption curve of J_2.

In addition to the absorption bands already noted, in the region of 400 $m\mu$ there is another very intense band, increasing with increasing KJ concentration and probably associated with the allowed transition

$$Co^{2+}J^- + h\nu = Co^+J.$$

In view of the presence of strong oxidizing agents in the nitrate melt, such a transition may promote oxidation of the J^- ion. Indeed, at 160° a solution of KJ

Fig. 4

Figure 4: Fig. 4

in the nitrate melt, subjected to the treatment described above,* is practically stable for a long time. In the presence of Co^{2+} ions in the melt, however, slow decomposition of KJ occurs with liberation of J_2. The rate of decomposition increases with increasing KJ concentration. Unfortunately, it was not possible to isolate this band, since the absorption band of J_2 is located in the same wavelength region.

Figure 3 shows part of the absorption curve of J_2 in the nitrate melt acidified for the decomposition of KJ.

Fig. 4. Solid-phase reactions in the systems $Co(NO_3)_2 \cdot 6H_2O$–KCl (1), $Co(NO_3)_2 \cdot 6H_2O$–KBr (2), $Co(NO_3)_2 \cdot 6H_2O$–KJ (3).

Figure 4 presents the absorption curves of samples obtained by pressing $Co(NO_3)_2 \cdot 6H_2O$ with potassium halides. Absorption was measured relative to a disk pressed from the corresponding potassium halide with an admixture of KNO_3. Even upon mixing crystals of $Co(NO_3)_2 \cdot 6H_2O$ with potassium halides, the pink color of the $Co(NO_3)_2 \cdot 6H_2O$ crystals changes⋯

to blue (the color of chloride and bromide complexes) or dark green (the color of iodide complexes). This reaction is at equilibrium, and the state of its equilibrium depends strongly on the temperature and humidity of the air and on the hygroscopicity of the potassium halide used. Therefore, in order to obtain the higher cobalt complexes, the mixture of crystals of $Co(NO_3)_2 \cdot 6H_2O$ with KCl and KJ was preliminarily dried at 30–50°. As expected, in this case higher halide complexes were formed, with an even content of halogen ions: $K_2[CoCl_4]$ and, possibly, $K_2[CoCl_2(NO_3)_2]$ at $\lambda = 690$ and ~ 630 mμ (curve 1), $K_4[CoBr_6]$ and $K_2[CoBr_4 \cdot 2H_2O]$ at $\lambda = 725$ and ~ 670 mμ (curve 2), $K_4[CoJ_6]$ and, probably, $K_2[CoJ_4 \cdot 2H_2O]$ at $\lambda = 782$ and ~ 700 mμ (curve 2). On curve 2 the right-hand shoulder of the intense band of the allowed transition is also visible; in this case it is not accompanied by oxidation of KJ, owing to the absence of electron acceptors. In Fig. 1 a weak band at 535 mμ is also visible, possibly attributable to $K_2[CoCl_6]$. The absence in Figs. 2 and 3 of the maxima found in solutions and melts at 695 mμ for the system with KBr and at 750 mμ for the system with KJ is additional confirmation of the existence in the liquid state of complex ions of composition $[CoX\Gamma_5]^{4-}$, where X is the solvent or the anion of the solvent melt, and Γ is J^- or Br^-.

Summarizing the study of the interaction of the Co^{2+} ion with halogen ions in a nitrate melt, it should be said that all the complexes investigated are formed exothermically, with increasing stability in the series Cl, Br, J. According to Lobaneva's data (^{3}), in acetone solutions the stability of complex halides of Co^{++} in terms of ΔF decreases in the series Cl, Br, J; the endothermicity decreases in the series Br, Cl, J, and ΔS compensates the endothermicity of complex formation. As can be seen, in the nitrate melt, owing to the exothermicity of the substitution processes of NO_3^- ions by halogen ions, the stability of the complexes follows the series of greatest energetic advantage.

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