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SPECTROPHOTOMETRIC STUDY OF CHLORIDE COMPLEXES OF COBALT IN MELTS

The study of the state of ions in melts is of great theoretical and practical importance, since molten salts constitute the most extensive class of inorganic solvents. Spectrophotometry has been a classical method for studying aqueous and nonaqueous solutions, and it should be expected that the application of this method to the molten state will lead to results no less useful. Practical work in this direction is only beginning ($^{1-5}$). However, spectrophotometry has not been applied with the use of physicochemical analysis methods; for this reason the value of the data from the corresponding measurements proves, to a certain extent, to be limited.

The present work is devoted to the study of chloro complexes of CO^{2+} in a melt of $LiNO_3$—KNO_3 of approximately eutectic composition.

The measurements were carried out on an SF-4 spectrophotometer that had a specially equipped cuvette compartment, consisting of a massive stainless-steel block (Fig. 1), five faces of which were surrounded by a heating coil. Holes were cut in the block: two round vertical ones for thermometers, or thermocouples; a square vertical one for the cuvette holder; and two through horizontal ones in mutually perpendicular planes (for the measured light beam and for introducing a device that changed the position of the cuvettes in the light path). From above, the block was closed with a heat-insulated stainless-steel cover. The side and bottom faces were heat-insulated with fireclay brick. The block was placed in a welded steel casing, between whose double walls thermostated water circulated. The casing was closed with a steel cover with double walls. Openings were provided in the walls and in the cover of the casing for passage of the light beam, movement of the cuvette holder, insertion of thermometers or thermocouples, and filling the block with inert gas. The cuvette compartment was rigidly fastened by a special bracket between the illuminator and the body of the spectrophotometer. With this arrangement of the cuvette compartment, any radiation, including the thermal radiation of the furnace, passes through the monochromator. Power was supplied to the furnace block through a voltage stabilizer, and constancy of temperature was maintained visually with an accuracy of ±1°C. The maximum operating temperature was 900°. Standard 10-millimeter quartz cuvettes were used for the work.

Fig. 1. Furnace block of the cuvette compartment of the spectrophotometer

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Fig. 2

Figure 2: Fig. 2

All reagents used were purified by double recrystallization, since even chemically pure substances are insufficiently transparent upon melting.

The solvent was an anhydrous mixture of 45 mol.% $LiNO_3$ and 55 mol.% KNO_3. The solvent was dehydrated with a stream of dry nitrogen passed

through the melt for 4 h at 220°. The ions Co^{2+} and Cl^- were introduced into the system in the form of $Co(NO_3)_2 \cdot 6H_2O$ and KCl. Preliminary experiments showed that small amounts of water and nitric acid present in the melt do not affect the absorption spectrum of $Co(NO_3)_2$ or of its chloride complexes. Thus, the introduction into the melt at 160° of up to 3% water (by volume) leads only to an effect associated with dilution of the solution. In all experiments the comparison cuvette contained the solvent and KCl in the same amounts in which the latter was present in the working solution. Measurements were carried out at 160, 200, and 240°. The experimental data are presented in Figs. 2, 3, and 4.

As can be seen from Fig. 2, the absorption spectrum of a 0.0248 M solution of $Co(NO_3)_2$ depends little on temperature. Only a slight shift of the absorption maximum toward the long-wavelength region is observed, in connection with weakening of the ligand field of the absorbing ion, and a slight broadening of the absorption band, caused by superposition of vibrational transitions. The partial weakening of the absorption intensity at the band maximum may to a considerable extent be associated with thermal dilution of the solution. At present many examples have been analyzed of splitting of the energy levels of the $3d^7$ configuration of the Co^{2+} ion in fields of various symmetry ([6]-[10]). Comparison of the absorption band shown in Fig. 2 with the nature of the absorption bands of various octahedral cobalt complexes suggests octahedral coordination of cobalt ions in the nitrate melt.

Fig. 2. Absorption spectrum of a 0.0248 M solution of $Co(NO_3)_2$ in a nitrate melt:
1 –240°; 2 –200°; 3 –160°

Fig. 3. Effect of complex formation on the absorption spectrum of a 0.00248

Fig. 3

Figure 3: Fig. 3

Fig. 4. Light absorption in the isomolar series of the 0.0248 mol/l system $Co(NO_3)_2$–K_2Cl_2: a–600 mμ; –630 mμ; –660 mμ. Temperatures: 1–160°; 2 –200°; 3–240°

Figure 4: Fig. 4. Light absorption in the isomolar series of the 0.0248 mol/l system $Co(NO_3)_2$–K_2Cl_2: a–600 mμ; –630 mμ; –660 mμ. Temperatures: 1–160°; 2–200°; 3–240°

M solution of $Co(NO_3)_2$ in a nitrate melt.
a –160°; b –200°; c –240°. Molar ratios KCl : $Co(NO_3)_2$:
1 –0; 2 –8; 3 –16; 4 –32; 5 –56; 6 –81; 7 –114; 8 –183; 9 –251; 10 –387; 11 –653; 12 –1160

melt. The shift of the band toward the long-wavelength region indicates a weakening of the ligand field of the octahedral nitrate complexes in comparison with the fields of such ligands as NH_3, H_2O, and MgO, and similarity to the field strength of such ligands as F^- and the oxygen of sulfuric and phosphoric acids.

Figure 3 presents the changes in the absorption spectrum of a 0.00248 M solution of cobalt nitrate associated with the formation of chloride complexes. As can be seen, with increasing concentration of potassium chloride there occurs a shift of the principal absorption band toward the long-wavelength region and the successive appearance of three new absorption maxima, corresponding

formation, respectively, of three types of complex ions. On the basis of numerous studies of cobalt complex chlorides in aqueous and nonaqueous solutions and in melts ([5]), it is generally accepted that the highest complex formed in these systems is $[CoCl_4]^{2-}$. Therefore, the appearance of the longest-wavelength maximum (690 mμ) may be associated with the formation of this ion. Indeed, this maximum appears at the highest KCl concentration, after the maximum at 625 mμ begins to decrease and that at 635 mμ undergoes considerable development. It is also characteristic that the position of the maximum at 690 mμ depends little on the nature of the solvent and on other features of the systems, which confirms the tetrahedral structure of the ion $[CoCl_4]^{2-}$ ([10,11]). The absorption band with a center of gravity near 625 mμ is due to one of the lower chloride complexes of cobalt. Application of the Bodländer-Abegg method ([12]) in the region of 660 mμ

Fig. 4. Light absorption in the isomolar series of the 0.0248 mol/l system $Co(NO_3)_2$–K_2Cl_2: *a*–600 mμ; *b*–630 mμ; *c*–660 mμ. Temperatures: 1–160°; 2 –200°; 3–240°.

at such KCl concentrations, when only the formation of complex species giving absorption with a maximum at 625 mμ can be expected, showed that under these conditions the molecular compound $CoCl_2$ is formed. Thus, the maximum at 625 mμ is associated with the existence of $CoCl_2$ species, and the maximum at 665 mμ is due to absorbing centers of composition $[CoCl_3]^-$. Using the same method, the dissociation constant of the molecular compound was estimated. Its order is $K_2 = 2 \cdot 10^{-2}$. It was not expedient to determine the temperature dependence of the instability constant of the complex, since the absorption bands of the different complex species overlap one another and absorption in the region of 660 mμ cannot be attributed to a single compound even at very low KCl concentrations. The general character of the dissociation of the chloride complexes of Co^{2+} with increasing temperature is clearly seen from Fig. 3. Since, at the same time, the positions of the absorption maxima do not change appreciably, the principal decrease in absorption with increasing temperature may be ascribed to dissociation of the complexes. Thus, chloride complexes in a nitrate melt are formed exothermically, which is fully consistent with the notion of the greater strength of chloride complexes in comparison with nitrate complexes. As is known, in aqueous and organic solutions ([13,14]) chloride complexes are formed with absorption of heat, and complex formation proceeds mainly through an increase in entropy.

Figure 4 presents data for the isomolar series in the system $Co(NO_3)_2$–K_2Cl_2 at a total concentration of 0.0248 M/l. The abscissa axis gives the values

$$n = \frac{C_{K_2Cl_2}}{C_{Co(NO_3)_2}},$$

where C is the concentration in moles per liter. The ordinate axis gives the differences between the optical density of the solution under investigation and the calculated value of the optical density due to absorption by cobalt ions. All concentration calculations were carried out for 160°, with the specific gravity of the melt taken as equal to 1.376.

1.94 g/cm^3 ([4]). The data of the isomolar series show that the principal dominant compound formed in the system is $CoCl_2$, $n = 1$. This is manifested most clearly at $\lambda = 600$ mμ.

With increasing wavelength, the maximum shifts toward the formation of compounds with a higher coordination number. At $\lambda = 660$ mμ the maximum becomes flat and extends over the range of values $n = 1$—2, i.e., in the region of complex compounds of composition $CoCl_2$–$[CoCl_4]^{2-}$. Thus, the data of the isomolar series confirm the conclusions stated earlier. The general increase in ΔD in the case of the data referring to $\lambda = 600$ mμ, as compared with the analogous values at $\lambda = 630$ mμ, is noteworthy. Evidently, this may be explained by the superposition of absorption by particles that disappear at high KCl concentrations (Fig. 3). Such particles, apparently, may be $CoCl^+$ ions.

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