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Absorption Spectra of Several 3d Transition Metal Ions in Molten Fluoride Solution^{1,2}

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The spectra of several 3d transition metal ions, Fe(II), Ni(II), Cr(II), and Cr(III), have been studied; these ions were dissolved in several molten fluoride salts which are essentially the stoichiometric mixture Li_2BeF_4 with and without excess F^- , as LiF . The spectra were obtained in the temperature range of 540–650°; the samples were contained in graphite windowless containers for the study. Fe(II) exhibits a peak and shoulder absorbance envelope with maximum absorbance at 9800 and 5500 cm^{-1} . Respective molar absorptivities are 4.5 and 3. The spectrum appears unaffected by change in solvent composition. The spectrum of Ni(II) at a temperature of 550° consists of three peaks at 23,100, 10,800, and ca. 6000 cm^{-1} . Respective molar absorptivities are 11, 2, and ca. 1. The spectrum appears to be likewise unaffected by solvent change. At a temperature of 550°, Cr(II) appears to exhibit one peak at 14,000 cm^{-1} with a molar absorptivity of 6; Cr(III) exhibits three peaks at 33,000, 22,600, and 14,500 cm^{-1} ; respective molar absorptivities are ca. 10, 10, and 7. The spectral results would suggest that these ions are situated in O_h symmetry in these melts with little tendency to change if the "free" fluoride ion concentration is reduced over the range studied. Fe(II) is a possible exception to this generality.

Introduction

Spectrophotometric studies of several transition metal ions, Fe(II), Ni(II), Cr(II), and Cr(III), dissolved in various molten fluoride salts over the temperature range 540–650° are summarized in this paper. The solvent salts include various compositions of $\text{LiF}-\text{BeF}_2$ (66:34, 77:28, and 60:40 mol %). The $\text{LiF}-\text{BeF}_2$ mixtures can be considered as solvents of the composition Li_2BeF_4 in which there is a stoichiometric excess or deficiency of fluoride ion. The spectra of all solutes were studied in the first solvent. The spectrum of Ni(II) was studied in all solvents. These studies were undertaken to obtain information about the coordination of solute species in these fluoride melts, to evaluate the effect of F^- excess or deficiency on this coordination, and to compare the spectral results with those previously obtained over a similar temperature range in an alkali fluoride melt, $\text{LiF}-\text{NaF}-\text{KF}$ (46.5:11.5:42 mol %).³ It was assumed that coordination changes of the solute species would be evident by changes in the position and/or intensity of the respective d-d spectral transitions as the solution environment was altered.

Experimental Section

The spectra were recorded by means of a Cary recording spectrophotometer, Model 14M. The molten salt samples were contained in captive liquid cells⁴ modified for nonwetting melts.⁵ The cells were made of graphite for these studies. They were loaded with chunks of solidified solvent plus solute fluoride, which were then melted, or with chunks of solidified salt solution

These solutions were prepared in graphite crucibles by mixing the desired components together; the salts were then melted in the presence of $\text{NH}_4\text{F} \cdot \text{HF}$ under an inert atmosphere of helium. Helium was also bubbled through the melt to mix the components and remove the $\text{NH}_4\text{F} \cdot \text{HF}$ after which the melts were quenched. In all cases, the samples were loaded in an inert-atmosphere box and each loaded cell was transferred to a heated cell assembly and melted without exposure to the atmosphere. The procedure for carrying out these operations and a description of the heated cell assembly has been given.⁶

The solvents were prepared by standard methods.⁶ After spectral study the samples were rapidly quenched and the solid sample was analyzed for solute content. In some instances, various portions of the solidified sample were analyzed separately to verify complete dissolution of the solute or to eliminate errors due to a precipitate or undissolved material.

In calculating molar absorptivities, the density of the $\text{LiF}-\text{BeF}_2$ solvent at the various temperatures was calculated by means of a previously reported formula.⁷ Densities of the latter solvents were estimated by the method of Cantor.⁸ The path length of the solutions contained in these modified captive liquid cells was determined by a measurement of the path length of the solidified salt sample in the container after the experiment. This measurement was then corrected for volume expansion on melting. Owing to the above estimation of liquid path length, the molar absorptivities calculated for these solutions are only considered accurate to within 10%.

Results

The spectrum of Fe(II) in $\text{LiF}-\text{BeF}_2$ (66:34 mol %) at a temperature of 540° is shown in Figure 1. The spectrum consists of two partially resolved peaks with maximum absorbance at 9800 and 5500 cm^{-1} . The respective molar absorptivities are 4.5 and 3. The

(1) Presented in part at the 155th National Meeting American Chemical Society, San Francisco, Calif., April 1968.

(2) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(3) J. P. Young and J. C. White, *Anal. Chem.*, **32**, 799 (1960).

(4) J. P. Young, *ibid.*, **36**, 390 (1964).

(5) J. P. Young, *Inorg. Chem.*, **6**, 1486 (1967).

(6) W. R. Grimes, D. R. Cuneo, F. F. Blankenship, G. W. Keilhotz, H. F. Poppendick, and M. T. Robinson, "Fluid Fuel Reactors," J. A. Lane, H. J. MacPherson, and F. Moslam, Ed., Addison-Wesley Publishing Co., Reading, Mass., 1958, p 584.

(7) Oak Ridge National Laboratory Molten Salt Reactor Program Semi-annual Progress Report, ORNL-4037, Aug 31, 1966, p 194.

(8) Oak Ridge National Laboratory Reactor Chemistry Division Annual Progress Report, ORNL-3913, Dec 31, 1967, p 29.

spectrum of Fe(II) in the same solvent at 650° again consists of two partially but less resolved absorption bands with maximum absorbances at 9600 and *ca.* 5800 cm^{-1} . Molar absorptivities are, respectively, 5 and 2. In the solvent LiF-BeF₂ (72:28 mol %), spectral measurements of Fe(II) were carried out only at 650° because of the higher melting point of the solvent. The positions and intensities of the absorption peaks for Fe(II) in this solvent were identical, within experimental error, with those seen in the former solvent at 650°.

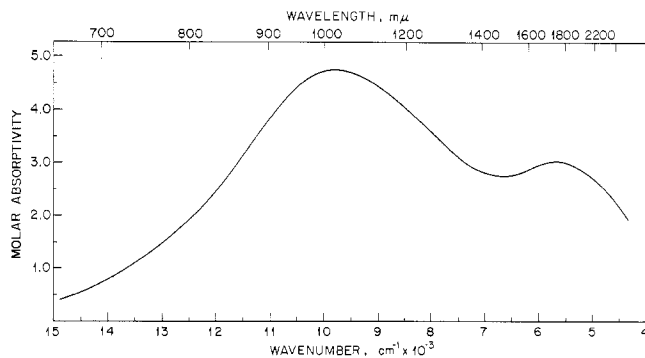


Figure 1.—Spectrum of FeF₂ in molten 2LiF · BeF₂ at 540°.

The spectrum of Ni(II) in LiF-BeF₂ (66:34 mol %) at 550° is shown in Figure 2. The spectrum consists of three spin-allowed d-d absorption peaks with maxima at 23,100, 10,800, and *ca.* 6000 cm^{-1} . The respective molar absorptivities of these peaks are 11, 2, and *ca.* 1. The latter peak at 6000 cm^{-1} is very broad and diffuse so that both its exact position and its intensity are difficult to determine. At a temperature of 650° there is essentially no change in the position of the absorptions. The molar absorptivities appear to be reduced slightly, under 10%, however, which is within the experimental errors of the technique. Again, as with the Fe(II) case, no change in spectra is observed in the LiF-BeF₂ (72:28 mol %) solution at a temperature of 650°. In yet another experiment, the positions and intensities of Ni(II) peaks in a melt of LiF-BeF₂ (60:40 mol %) at 550° were the same, within experimental error, as those seen in the first solvent at 550°.

The spectrum of Cr(II) in molten LiF-BeF₂ at 550°, shown in Figure 3, consists of one broad absorption peak at 14,000 cm^{-1} . The molar absorptivity is 6 at the peak maximum. The edge of yet another absorption band can be seen at higher energies. This is believed to be a charge-transfer band, but has not been characterized further.

The spectrum of Cr(III) in LiF-BeF₂ at 550°, Figure 4, consists of three peaks at 33,000, 22,600, and 14,500 cm^{-1} . The respective molar absorptivities of these peaks are *ca.* 10, 10, and 7. The first peak fuses with a more intense ultraviolet peak which again may be a charge-transfer type within the Cr-F coordination. The intense ultraviolet absorption was sub-

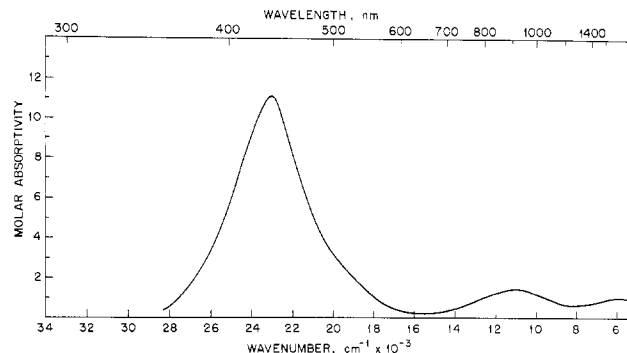


Figure 2.—Spectrum of NiF₂ in molten 2LiF · BeF₂ at 550°.

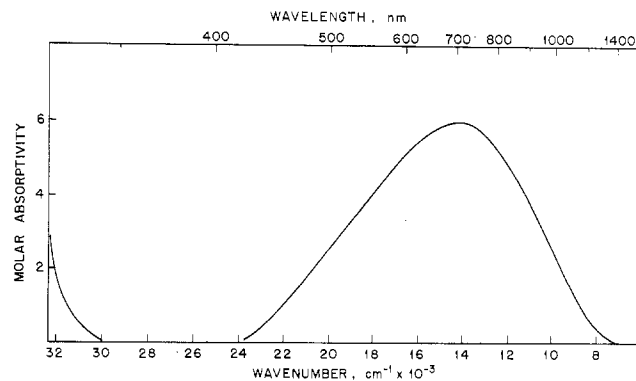


Figure 3.—Spectrum of CrF₂ in molten LiF · BeF₂ at 550°.

tracted from the spectral trace; the region where this was necessary is shown as a dashed line in Figure 4. Because of the interference and resultant correction, the accuracy of both the position and intensity of this particular transition could be affected.

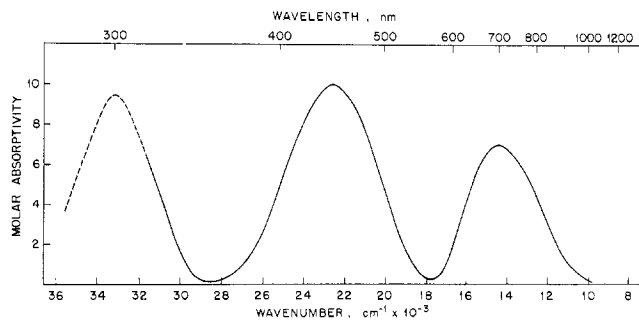


Figure 4.—Spectrum of CrF₃ in molten LiF · BeF₂ at 550°.

Discussion

From the spectra shown in the figures, a general observation can be made that these solute ions tend to be octahedrally coordinated in these fluoride melts. Fe(II) appears to be an exception, however.

Octahedrally coordinated Fe(II), a 3d⁶ ion, should exhibit one spin-allowed transition⁹ in the region of 10,000 cm^{-1} . Iron(II) is an example of an ion whose

(9) Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **13**, 880 (1954).

coordinating ligands are distorted by a dynamic Jahn-Teller effect.¹⁰ The melt spectrum demonstrates this distortion. Hatfield and Piper show a difference of 3670 cm^{-1} for the separation of the peak and shoulder in the crystalline spectrum of FeF_2 at room temperature.¹⁰ The same separation in the melt spectrum is 4300 cm^{-1} . It is interesting to note that the spectrum of FeF_2 dissolved in molten LiF-NaF-KF (525°) is similar to that seen in this work.¹¹ No molar absorptivities were calculated for the alkali fluoride melt, but the intensities were weak and the ratio of the intensity of the two peaks was the same as that given here.

Octahedrally coordinated Ni(II) , a $3d^8$ ion, would be expected to exhibit three spin-allowed transitions⁹ in the regions seen in Figure 2. These spectral results are similar to those reported for the spectrum of Ni(II) in molten LiF-NaF-KF where this solute species is believed to be in O_h symmetry.¹²

The spectrum of Cr(II) , a $3d^4$ ion, in O_h symmetry should exhibit one spin-allowed absorption peak⁹ in the region of $14,000\text{ cm}^{-1}$. In the solid state, it has been shown by X-ray analysis that Cr(II) in crystalline CrF_2 is situated within a tetragonally distorted octahedron, with two F^- at 2.43 \AA , two F^- at 2.01 \AA , and two F^- at 1.98 \AA .¹³ The reflectance spectrum of CrF_2 in the solid state at room temperature^{14,15} exhibits a complex peak-shoulder type of envelope which indicates a splitting of the single spin-allowed transition because of the lower symmetry. The shoulder seen in the solid CrF_2 spectrum is lost in the melt spectra. It would appear, therefore, that the distortion of solid CrF_2 is removed in the melt and that Cr(II) in molten LiF-BeF_2 exists in O_h symmetry.

The spectrum of Cr(III) , a $3d^3$ ion, exhibits three spin-allowed d-d transitions⁹ in the energy regions where they should be found if the ion were situated in O_h symmetry in these melts. In the first spectral studies of fluoride melts, Cr(III) in molten LiF-NaF-KF was observed to have peaks at $14,500$ and $22,500\text{ cm}^{-1}$.³ No attempt was made at that time to look for the highest energy peak.

As stated earlier, part of the purpose of this study was to investigate any alteration of the spectra of these solute species as the fluoride solvent was altered from a solvent that could be considered to be close to molten Li_2BeF_4 (66.6 mol % LiF -33.3 mol % BeF_2). In this study the LiF concentration was varied over

the range of 72-60 mol %, corresponding to an excess or deficiency of free F^- compared to Li_2BeF_4 . As pointed out, the spectra were also compared with previous work, where possible, carried out in an alkali fluoride solvent^{3,11,12} where the solvent F^- should be relatively free. In all cases, within the apparent experimental errors of the method, only spectral changes associated with thermal effects can be noted. Over rather large changes in solvent composition, the spectra are unaffected. It would seem not only that these ions, except for Fe(II) , prefer O_h symmetry in fluoride melts but also that this coordination is maintained as the solvent is altered as described in these experiments. One is tempted to say that O_h coordination may be preferred generally by transition element ions. This conclusion is not too surprising in alkali fluoride melts if one considers the size and electronegativity of the fluoride ion. The fact that the coordination appears the same, also, in melts corresponding empirically to an equivalence or deficiency of fluoride ion¹⁶ with respect to BeF_4^{2-} is puzzling. Although possible, it does not seem likely that the BeF_4^{2-} grouping unsuccessfully competes with a larger Z/R transition element ion for F^- (Z being the atomic number and R the ionic radius). It is perhaps more likely that BeF_4^{2-} can be treated as a ligand which somehow interacts with the solute ions in a manner which preserves their O_h symmetry. A third possibility to explain all cases arises from a statement Jørgensen¹⁷ attributed to Pauling in which Pauling suggested that the fluoride ion can donate, relatively, so little electron density in the form of bonding orbitals to a central metal ion that a high coordination number (6 or 8) is preferred. Activity coefficients of LiF in various mixtures of molten LiF-BeF_2 ¹⁶ would tend to question this possibility as the data suggest that the F^- is being tied up by Be(II) , at least in the solvent alone. On the basis of the present results, the best explanation for the constancy of spectra as the solvent is altered is that the BeF_4^{2-} grouping does indeed coordinate with these ions in a way to maintain O_h symmetry. The case of Fe(II) is the poorest example of simple coordination, even in the alkali fluorides, and this ion is probably distorted by dynamic Jahn-Teller effects. Another example of a Jahn-Teller ion is Cr(II) ; the spectral results indicate that the dissolution of CrF_2 in a molten fluoride salt certainly reduces the distortion.

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(10) W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, 3, 1295 (1964).

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(13) S. Geller, Ed., Section II, "Inorganic Compounds," in "Structure Reports," Vol. 21, W. B. Pearson, Ed., N. V. A., Oosthoek's Uitgevers Mij, Utrecht, 1964, p 204.

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(15) It can also be noted that $\text{Cr(H}_2\text{O)}_6^{3+}$ at room temperature exhibits a peak-shoulder type of spectra in which four transitions have been indicated by mathematical resolution: J. P. Fackler and D. G. Holah, *Inorg. Chem.* 4, 954 (1965).