OBSERVATIONS ON THE ABSORPTION SPECTRA OF THE RARE EARTHS. II.

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The absorption spectra give invaluable clews in the rapid estimation of the coloured rare earth salts since we have no other satisfactory chemical means of detecting the elements of this family. The bands, however, are often changed both in positions and in intensities by change in the conditions under which observations are made, e.g., by changing concentration or by adding other substances. The spectra should therefore be used with the utmost caution only for the qualitative purpose. In the first paper of this series(1) the writer has pointed out that the bands of neodymium nitrate and also of praseodymium nitrate are shifted toward the longer wave-lengths when they are dissolved in some organic solvents, the shifts increasing as the dielectric constant of the liquid decreases. The present work was undertaken with the object of obtaining further knowledge as to the shifts of the bands of neodymium salts.

Experimental.

Material and Apparatus. The neodymium oxide used was the same one as used in the previous work. It was Prof. Rolla's preparation and of 99.99% purity. Each spectrum was photographed by a constant deviation spectrograph constructed in the workshop of the Institute of Physical and Chemical Research, Tokyo. As the source of illumination a tungsten lamp was used. The solutions were held in a glass tube, 5 or 10 cm. in length, provided with glass end plates.

Absorption of $Nd(NO_3)_3$ and $NdCl_3$ in Various Solvents. It has long been known that in some cases different salts of the same element yield bands of different wave-lengths when dissolved in the same solvent. The absorption of the aqueous solution of neodymium nitrate, for example, is a little different from that of neodymium chloride at a certain higher concentration(2). This is supposedly due to the fact that the negative field produced by the nitrate ion differs in intensity from that produced by the chloride ion so that the electron shells of the neodymium ion are deformed in a more or less different manner in each case.

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(1) This Bulletin, **6** (1931), 147.

(2) *Proc. Camb. Phil. Soc.*, **12**, 206.

As reported in the previous paper the oppositely charged ions are brought closer to one another with considerably marked changes of the bands when the salt is dissolved in a liquid of low dielectric constant. It seems now probable that nitrate and chloride of neodymium might produce different spectra, if dissolved in such a liquid, even at such a low concentration that they might produce similar spectra if dissolved in water. An attempt was therefore made to compare the spectra of neodymium chloride and nitrate dissolved in alcohol and in other organic solvents.

In each case 0.1 gr. of neodymium oxide was dissolved in nitric or hydrochloric acid and excess acid then removed. As the chloride is less soluble in those organic solvents used than the nitrate, each salt was first dissolved in 6 c.c. of water and the volume of the solution was made up to 50 c.c. with the individual solvent, i.e., ethyl alcohol etc. The spectra of the chloride and the nitrate in the same solvent were then compared.

Fig. 1 shows the spectra of the salts dissolved in water. A represents the absorption of the chloride and B that of the nitrate. At this concentration (0.0119 mol.) both are practically identical. Fig. 2 shows the spectra of glycerol solutions. The two are with difficulty distinguishable. Of the methyl alcohol solutions, however, the bands of the nitrate are shifted more markedly than those of the chloride, in spite of the concentration with respect to Nd^{+++} being exactly the same as before. In the ethyl alcohol solutions the difference is as plain as in the methyl alcohol solutions. These two cases are shown in Figs. 3 and 4. The difference becomes more conclusively apparent when the acetone solutions are examined. As shown in Fig. 5, the band in the 5750 Å region of the nitrate is unmistakably spread out and shifted nearly 45Å toward the red as compared with the same band of the chloride. In the nitrate solution the band at 5220Å and that at 4275Å are both shifted more redward and the two bands in the 5100Å region merge into one another. Comparison was also made with the concentrated aqueous solutions (0.476 mol.) in which case the nitrate likewise develops greater displacements than the chloride. (Fig. 6)

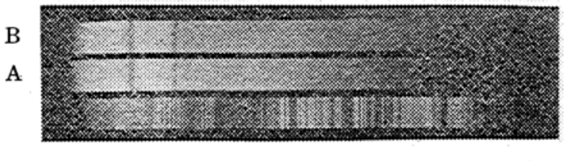

Fig. 1.—The absorption spectra of neodymium chloride (A) and nitrate (B) dissolved in water. (0.0119 mol., 10 cm.)

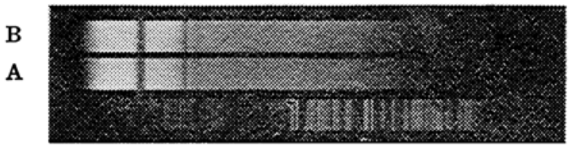

Fig. 2.—The absorption spectra of neodymium chloride (A) and nitrate (B) dissolved in glycerol. (0.0119 mol., 10 cm.)

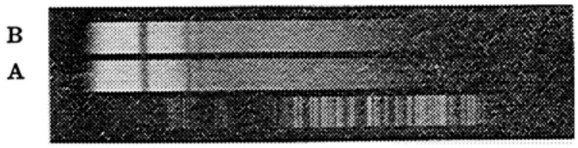

Fig. 3.—The absorption spectra of neodymium chloride (A) and nitrate (B) dissolved in methyl alcohol. (0.0119 mol., 10 cm.)

Fig. 4.—The absorption spectra of neodymium chloride (A) and nitrate (B) dissolved in ethyl alcohol. (0.0119 mol., 10 cm.)

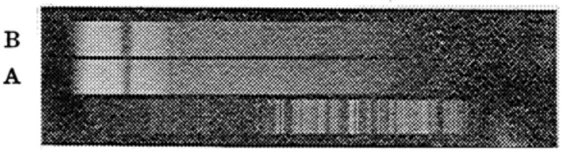

Fig. 5.—The absorption spectra of neodymium chloride (A) and nitrate (B) dissolved in acetone. (0.0119 mol., 10 cm.)

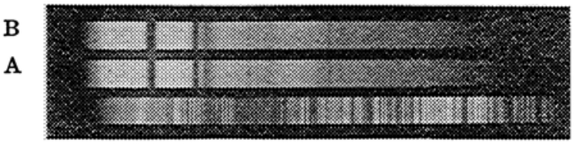

Fig. 6.—The absorption spectra of neodymium chloride (A) and nitrate (B) dissolved in water. (0.476 mol., 1 cm.)

Changes of the Bands of $Nd(NO_3)_3$ produced by Ether, Benzene etc. It was next desired to examine possible changes of the bands to be observed when neodymium nitrate was dissolved in a liquid having a dielectric constant lower than those used in the previous experiments. For this purpose ether, benzene, carbon tetrachloride and chloroform were used. Neodymium nitrate, however, is practically insoluble in these solvents when the liquids are used in the pure state. Each solvent was therefore mixed with ethyl alcohol to a certain ratio and then in the mixture the salt was dissolved. In Fig. 7, A and C represent the spectra of $Nd(NO_3)_3$ in pure ethyl alcohol while B that in the mixture ethyl alcohol + ether (1 : 4 by volume). In the latter solution, the band in the 5750 Å region is intensified and shifted slightly toward the red, the same band in the former solution being taken as standard. The band at 5220 Å is also shifted in some measure toward the red in the mixed solvent.

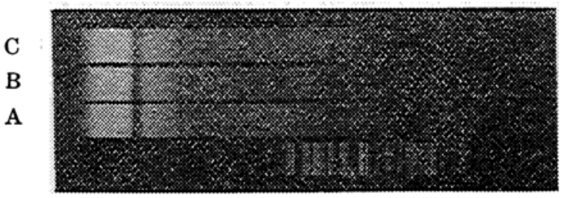

Fig. 7.—The absorption spectra of neodymium nitrate dissolved in ethyl alcohol (A and C) and in ethyl alcohol+ether (B). (0.0119 mol., 5 cm.)

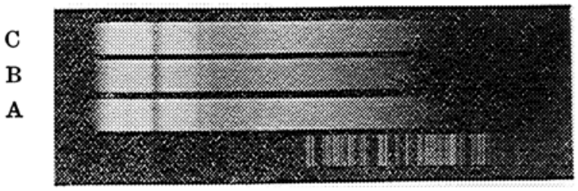

Fig. 8.—The absorption spectra of neodymium nitrate dissolved in ethyl alcohol (A and C) and in ethyl alcohol+benzene (B). (0.0119 mol., 5 cm.)

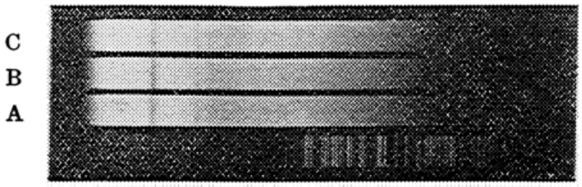

Fig. 9.—The absorption spectra of neodymium nitrate dissolved in ethyl alcohol (A and C) and in ethyl alcohol+carbon tetrachloride (B). (0.0119 mol., 5 cm.)

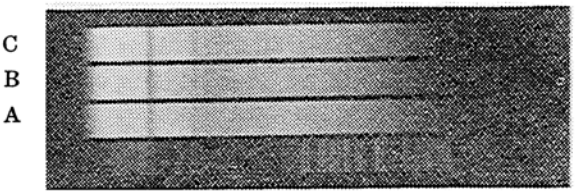

Fig. 10.—The absorption spectra of neodymium nitrate dissolved in ethyl alcohol (A and C) and in ethyl alcohol+chloroform (B). (0.0119 mol., 5 cm.)

The next examination was made with the ethyl alcohol-benzene solution. It was very interesting to find in the mixed solvent that the displacements of the bands in the 5750 Å region and at 5220 Å are slightly smaller or, in other words, that these two bands were shifted less redward than in the pure alcohol. Similar changes, i.e., the displacements of the bands toward the blue, were observed when the mixture of ethyl alcohol and carbon tetrachloride or ethyl alcohol and chloroform was used instead of pure ethyl alcohol. The concentration of the solutions was always 0.0119mol. and the observations were carried out through a depth of 5 cm. of the solutions. The results are shown in Figs. 8–10.

Discussion.

Neodymium chloride and nitrate when dissolved in a solvent of low dielectric constant show a marked difference even at rather a low concentration. This is exactly what has been expected and the fact that the difference becomes more apparent with decreasing dielectric constant of solvents indicates well that the shifts are to be produced by the field of the nitrate or other anion. The changes observed with the concentrated aqueous solution confirm this view as well.

The solvation of ions has not been taken into account in the interpretation so far. However, the changes of the bands observed when benzene, carbon tetrachloride or chloroform was mixed with ethyl alcohol in which neodymium nitrate was dissolved seem to be better explained by presuming that the solvent molecules play a part in this phenomenon. D. M. Murray-Rust and others state as to the solvation of ions and its relation to ionic dissociation(1):

"． . . . .The solvent therefore affects the conductivity of an electrolyte dissolved in it in a variety of ways. First, by the magnitude of its dielectric constant it determines the force of attraction between the ions

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(1) *Annual Rep., Chem. Soc.*, **27** (1930), 357.

and the energy needed to separate them. Then, the solvation of the ions appears to exert a decisive influence on the extent to which they form ion pairs or undissociated molecules, and in this respect the power of the solvent molecules to co-ordinate with both ions appears to be even more important than their dipole character. . . . ."

It is no doubt true that the neodymium ion is surrounded by molecules of water in which the salt is dissolved. That neodymium nitrate or chloride forms hexahydrate in the solid state suggests some of those water molecules being held in the solution by co-ordinate linkage. In addition to any molecules thus chemically combined, there may be a layer of molecules oriented by their own dipole character and it is difficult to distinguish in which state the solvent molecules exist in the neighbourhood of the neodymium ion. This question shall be put aside awhile as it is not very important to ascertain this in the present discussion. It is by all means possible, however, that the water molecules exert *some* influence over the neodymium ion. Thus in a concentrated solution, a deformation of the electron shells of the neodymium ion is brought about not only by the nitrate ion but also by the water molecules while in a dilute solution this is done mainly by the water molecules.

When dissolved in ethyl alcohol, the nitrate ion will come nearer to the neodymium ion than in the case of water solution. But as is well known this solvent still has the tendency of forming solvate and its molecules have dipole character so that the neodymium ion should never be quite free from the solvent molecules. In other words, the neodymium ion is, in the alcoholic solution, subjected to the combined force of the nitrate ion and the alcohol molecules. Consequently the bands are shifted in great measure toward the red.

What will happen then when the salt is dissolved in a mixture of ethyl alcohol and benzene? Benzene being a normal liquid has no tendency of associating with solute and is actually non-polar. Consequently benzene molecules behave rather indifferently in this case by which is meant that the neodymium ion is left under the influence of the nitrate ion and the alcohol molecules. In this solution the number of alcohol molecules in question should be much smaller so that the bands are shifted as a matter of course less redward. The same interpretation may be made for the changes of the bands observed in the case of alcohol-carbon tetrachloride and alcohol-chloroform mixtures. Ether is known to have abnormal properties though it is a normal liquid in the pure state and it is therefore no wonder that the shifts increase when ether is mixed with alcohol.

In conclusion it is suggested from the present investigation that the displacements of the bands of neodymium salts are produced by solvent molecules as well as by the nitrate or other anion.

Summary.

1. The absorption spectra of chloride and nitrate of neodymium in various organic solvents were compared.

2. The changes of the bands of neodymium nitrate produced by adding a normal liquid to the alcoholic solution were examined.

3. It is suggested that the absorption bands of neodymium salts are shifted by solvent molecules as well as by the anion.

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