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

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It has been confirmed by several investigators that the absorption bands of neodymium shift toward the longer wave-lengths by increasing the concentration and Beer's law holds only from a definite concentration down. Selwood(1) recently observed that for neodymia and other rare earths investigated increasing concentration is accompanied by a change of molecular volume and molecular refraction and a slight shift of absorption bands. He explained the phenomenon on the basis of the theory of the deformation of the electron shells. It is also well known that the bands of neodymium salts are shifted toward the red on the addition of a common ion. As Quill and Selwood with Hopkins(2) have concluded there may be more than one influence to deal with the phenomenon but the changes of the bands produced here may be possibly attributed to the deformation of the electron shells again since the shifts become more apparent with increasing amount of a common ion added. Changes somewhat similar to those produced on the addition of a common ion are expected to appear if the oppositely charged ions, i.e., Nd^{+++} and NO_3^- for example, are brought close enough to one another to cause distortion of the electron arrangement by any other means than changing concentration or adding a common ion and this will be performed by using a solvent having a smaller dielectric constant than water. Jones(3) studied the absorption spectra of the solu-

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(1) *J. Am. Chem. Soc.*, **52** (1930), 3112, 4308.

(2) Ibid., **50** (1928), 2929.

(3) Carnegie Institution of Washington Publication, No. 130, No. 160.

tions of the rare earths and some other comparatively rarer elements and suggested the formation of solvates. No observations were made, however, as to the existence of any general relation between the changes of the bands and the nature of the solvents used. H. Schaeffer⁽¹⁾ states that the absorption spectra of the rare earths are influenced by solvents, both organic and inorganic, and the displacements of the bands caused by the solvents with the lowest refractive indices are in general the greatest. Schaeffer's experiments were carried out with neodymium and didymium. Didymium is as well known a mixture of impure neodymium and praseodymium while neodymium used in his investigation is not believed to be absolutely free from other earths. It was therefore desired in the present investigation to examine conclusively if the changes of the bands are connected with any properties of the solvent used when the observations are made with pure neodymium.

Experimental.

The spectra were photographed by a Hilger spectrograph of constant deviation type and also by a Zeiss hand spectroscope combined with a camera, using a tungsten incandescent lamp as the source of illumination. A Baly absorption tube with quartz end plates was used throughout. The neodymium and praseodymium were purchased from Adam Hilger Ltd. They are the oxides prepared by Luigi R lla and believed by him to have not more than 0.01% total impurities.

Neodymium- and praseodymium nitrates in various organic solvents.

Nitric acid was added to 0.15 gr. pure neodymium oxide until the latter completely dissolved. After the excess of the acid was removed by evaporation the salt was dissolved in water and diluted to 50 c.c. The same amount of the oxide was converted into nitrate in the similar way and the salt dissolved in 50 c.c. pure acetone, thus the concentration of the two solutions being exactly the same, i.e., 0.019 mol. When these two solutions were compared with the spectrograph, there were observed in the acetone solution unmistakable broadenings and shifts of the bands toward the red. As will be seen in Fig. 1, the band at 5800 Å region becomes so markedly intensified in the acetone solution that one may take it more concentrated with respect to neodymium than the water solution. Again a series of nitrate solutions was prepared, using glycerol, methyl alcohol, ethyl alcohol and acetone as

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(1) *Physik. Z.*, **7** (1906), 822.

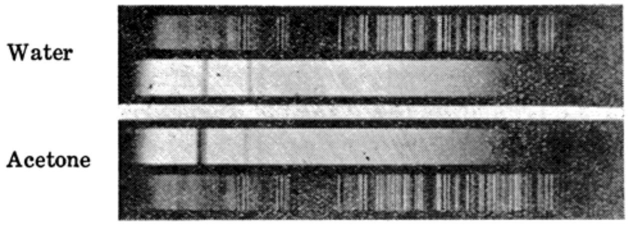

Fig. 1. Absorption bands of neodymium nitrate.

solvent respectively and their spectra were examined. Since each of them contains 0.15 gr. of neodymium as oxide, their concentrations should be the same while their bands are as shown in Fig. 2 more or less shifted and diffused toward the red. All these photographs were taken through 25 mm. of the solutions.

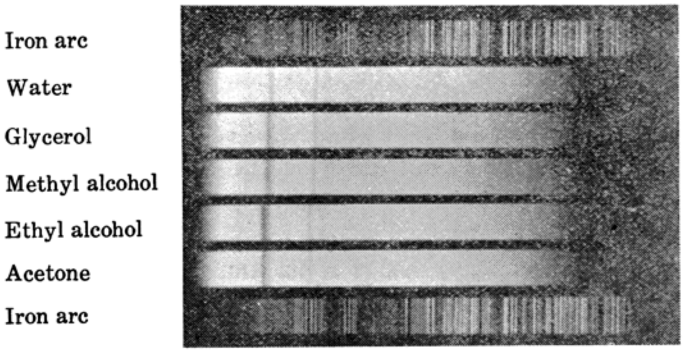

Fig. 2. Absorption bands of neodymium nitrate dissolved in various solvents.

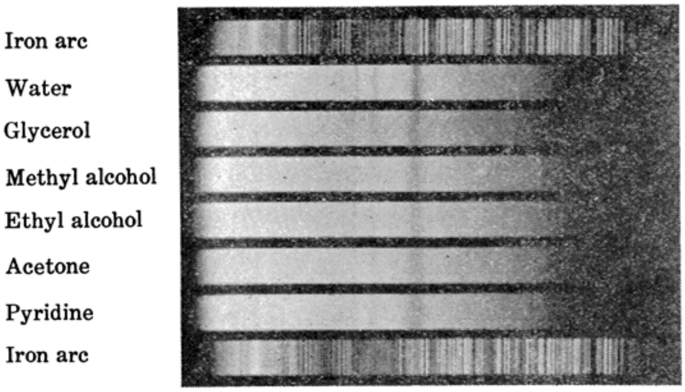

Fig. 3. Absorption bands of praseodymium nitrate dissolved in various solvents.

The similar effect was observed with praseodymium. Fig. 3 shows the absorption bands of praseodymium nitrate in water, glycerol, methyl alcohol, ethyl alcohol, acetone and pyridine respectively. Each solution contains 0.15 gr. of praseodymium as oxide and the spectrograms were taken through 30 mm. of the solution. The displacements are not so distinct as with neodymium but all the bands are more or less broadened and diffused, the effect being most pronounced in the acetone and pyridine solutions. The shift of the narrow band at 4819 Å can be most easily observed.

Influence of common ion in acetone solution.

It was next desired with interest to examine the influence of magnesium nitrate on the bands of neodymium nitrate in the acetone solution. As reported in the paper of Quill and others⁽¹⁾ magnesium nitrate as well as nitric acid produces a marked effect of displacing the bands of neodymium nitrate toward the red. Fig. 4 shows the shifts produced by magnesium nitrate in the water solution, the concentration of which is 0.012 mol. with respect to neodymium and 0.496 mol. with respect to magnesium. The photographs were taken through a depth of 70 mm. When acetone is used as solvent, the broadenings take place in the presence of magnesium nitrate in a slightly different manner. The solution contains the same amount of neodymium and magnesium and was photographed through the same depth as before, i.e., 70 mm., while all the bands are more or less broadened and above all the band at 5750 Å region is unmistakably spread out on both sides.

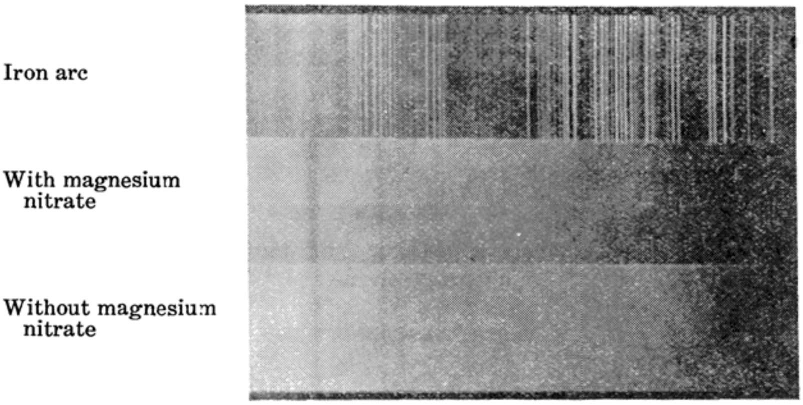

Fig. 4. Absorption bands of neodymium nitrate dissolved in water.

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(1) loc. cit.

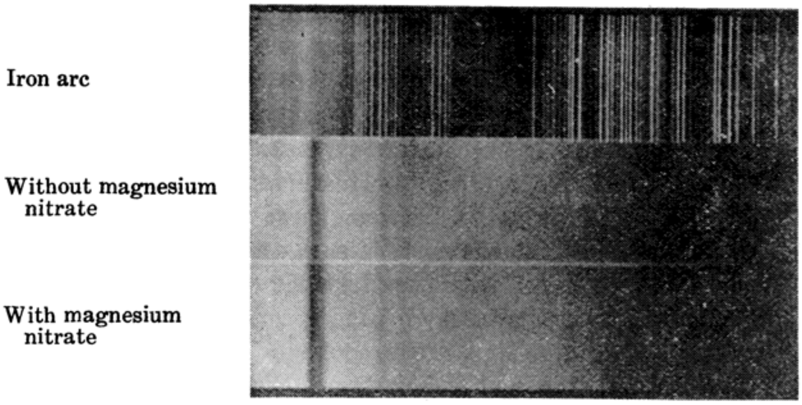

Fig. 5. Absorption bands of neodymium nitrate dissolved in acetone.

Discussion.

It was found in the present investigation that the displacements of neodymium bands are most pronounced when acetone or ethyl alcohol is used while the shifts produced by methyl alcohol or glycerol are less marked, the effect of the latter being the smallest. In the accompanying table are shown the displacement of the bands at 5800 Å in various solvents and the refractive indices of these solvents. No regularity can be observed between these two quantities, however.

Table

Solvent	Shift of the band at 5800 Å region (1)	Refractive index (20°C) (2)	Dielectric constant (20°C) (3)
Water	0	1.333	80.0
Glycerol	17 Å	1.4729	43.0
Methyl alcohol	26 Å	1.329	33.7
Ethyl alcohol	43 Å	1.361	25.7
Acetone	43 Å	1.3591	21.4
Pyridine	—	1.509	12.5

The oppositely charged ions may approach to one another with decreasing dielectric constant of the solvents in which they dissolve. If the defor-

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(1) The measurements are approximate as the edges are diffused.
(2) International Critical Tables, Vol. I.
(3) ibid., Vol. VI.

mation of the electron shells should cause the changes of the absorption bands, these changes might be the greatest when the solvent with the largest dielectric constant is used. The present investigation shows that this is exactly the case. As shown in the third column of the table, the dielectric constants decrease as the shifts increase. No photometric examinations were made with the spectrograms taken and it seems rather hasty to postulate any quantitative relation between these two quantities. In view of what has been observed, however, it is suggested that the displacement produced is possibly connected with the dielectric constant of the solvent.

Addition of magnesium nitrate to the acetone solution of neodymium nitrate produces a considerable change, not similar but slightly different from that produced in the water solution. Dissociation of neodymium nitrate as well as magnesium nitrate is supposed to be very small in the acetone solution and the effect of magnesium nitrate thus added may greatly differ from that of the so-called "common ion" added to the dilute water solution. It is still probable that the salt added may affect the electron arrangement of neodymium somehow so that it produces a change in the absorption spectra. It is known that for a given normality the changes produced by magnesium nitrate are slightly more pronounced than those produced by nitric acid. This fact suggests that a metal ion, dissociated or undissociated, might play a part. The further investigation is under way with the intension of finding the influence of foreign substances on the bands of neodymium.

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