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## Ions of Europium Distributed Between Different Configurations in Homogeneous Solutions

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Changes in the environment of europium ions in solution bring about changes in the structure of the absorption spectrum. For example, an aqueous solution of europium chloride upon having potassium nitrate added to it gives rise to the structures in the spectra of europium nitrate, in addition to the spectrum of europium chloride. Structures in the spectra of europium salts in alcohol differ from those in water. In a mixed solvent of water and alcohol both spectra are present with relative intensities which vary according to the relative amounts of the components. Europium chloride in the mixed solvent has a spectrum which cannot be distinguished from the exact superposi-

tion of the spectra of europium chloride in pure water and in pure alcohol. However, the spectrum of europium nitrate in the mixed solvent has its lines shifted from the positions they occupy in the spectra of the nitrate in the pure solvents. The shifts seem to vary continuously with the proportions of water to alcohol. Nevertheless, the lines remain sharp as successive amounts of water are added, with no suggestion that the lines are a blur, between the spectra of the limiting concentrations. The implications of these results are briefly discussed in their bearing upon the behavior of electrolytes in mixed solvents.

THE salts of europium in solution are not alike in the detailed structures of their absorption spectra and a particular salt gives rise to different spectra when it is dissolved in different solvents. In many instances, structures in the spectra can be resolved into lines, the numbers of which have been interpreted as representing the symmetry of the electrical fields about the europium ions.<sup>1, 2</sup> According to theory, a line in the spectrum of an ion in an electrical field is generally decomposed into a group of lines by fields of lower symmetry. Bethe<sup>3</sup> has derived the numbers of components into which a particular energy level will be decomposed. That the groups of lines in the spectra may be ascribed to this origin is supported by the facts, (a) salts of europium are strongly dissociated electrolytes.<sup>4</sup> The magnetic susceptibilities also show that trivalent europium is ionic in its salts,<sup>5, 6</sup> with  ${}^7F$  for its basic state; (b) when ions of a rare earth are present in crystals of different symmetry, the structures in the spectra differ in the same way as those of the different solutions of europium.

We shall as in previous publications confine

the discussion mainly to europium chloride and europium nitrate since they illustrate the phenomena we are to consider, deferring to later communications the behavior of other salts. The salts of europium were prepared from the oxalate kindly furnished us in a very pure state by Dr. H. N. McCoy. We wish to acknowledge here our great indebtedness to him.

In this communication we shall consider solutions which give rise to several spectra at the same time. Such solutions consist of a salt of europium dissolved in a homogeneous liquid phase of two components. An instance is already known where two absorption spectra appear when the solvent consists of only one component—europium nitrate dissolved in water. The relative intensities of these spectra vary with the concentration. The group in the spectrum at about 4650Å consists of a triplet in the range of concentrations from about 1.5 *M* to 0.01 *M*. This triplet shall be referred to as the nitrate-triplet. On further dilution an additional spectrum makes its appearance, with a quartet as its structure at about 4650Å and it gains in relative intensity as dilution proceeds. At 0.0007 *M* there is scarcely a trace left of the nitrate-triplet. This quartet we shall call the chloride-quartet because it occurs in the spectrum of europium chloride in aqueous solution, remaining practically unaffected by dilution in the range investigated—1.5 *M* to 0.0007 *M*.

<sup>1</sup> S. Freed and S. I. Weissman, *J. Chem. Phys.* **6**, 297 (1938).

<sup>2</sup> S. Freed and H. F. Jacobson, *J. Chem. Phys.* **6**, 654 (1938).

<sup>3</sup> H. Bethe, *Ann. d. Physik* **3**, 133 (1929).

<sup>4</sup> I. M. Klotz, *J. Chem. Phys.* **6**, 907 (1938).

<sup>5</sup> J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford, 1932), pp. 243, 246.

<sup>6</sup> H. Decker, *Ann. d. Physik* **79**, 324 (1926).

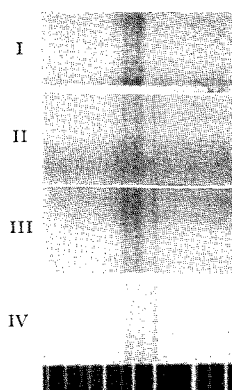


FIG. 1. Solution of 0.003 mole europium chloride in 150 cc water to which was added, I, 0.25 g  $\text{KNO}_3$ ; II, 0.50 g  $\text{KNO}_3$ ; III, 0.78 g  $\text{KNO}_3$ ; IV, pure europium nitrate in water.

When a little potassium nitrate was added to an aqueous solution of europium chloride, besides

the chloride-quartet of the latter, the nitrate-triplet appeared, unaccompanied by any other structures in the group at 4650A (see Fig. 1). The intensity of the nitrate-triplet seemed no greater than that which originates from a solution of europium nitrate containing the same concentration of nitrate as was furnished by the potassium nitrate. Hence no definite assertion can be made that the chloride ions cooperate with the nitrate ions in producing the nitrate-triplet. When the nitrate ion concentration was increased until it equaled that of the chloride ion, the chloride-quartet seemed almost entirely suppressed.

When anhydrous europium nitrate was dissolved in anhydrous ether, two strong lines occupied the place of the nitrate-triplet.<sup>1</sup> The question naturally arose—what modifications would occur in the spectrum when water is added

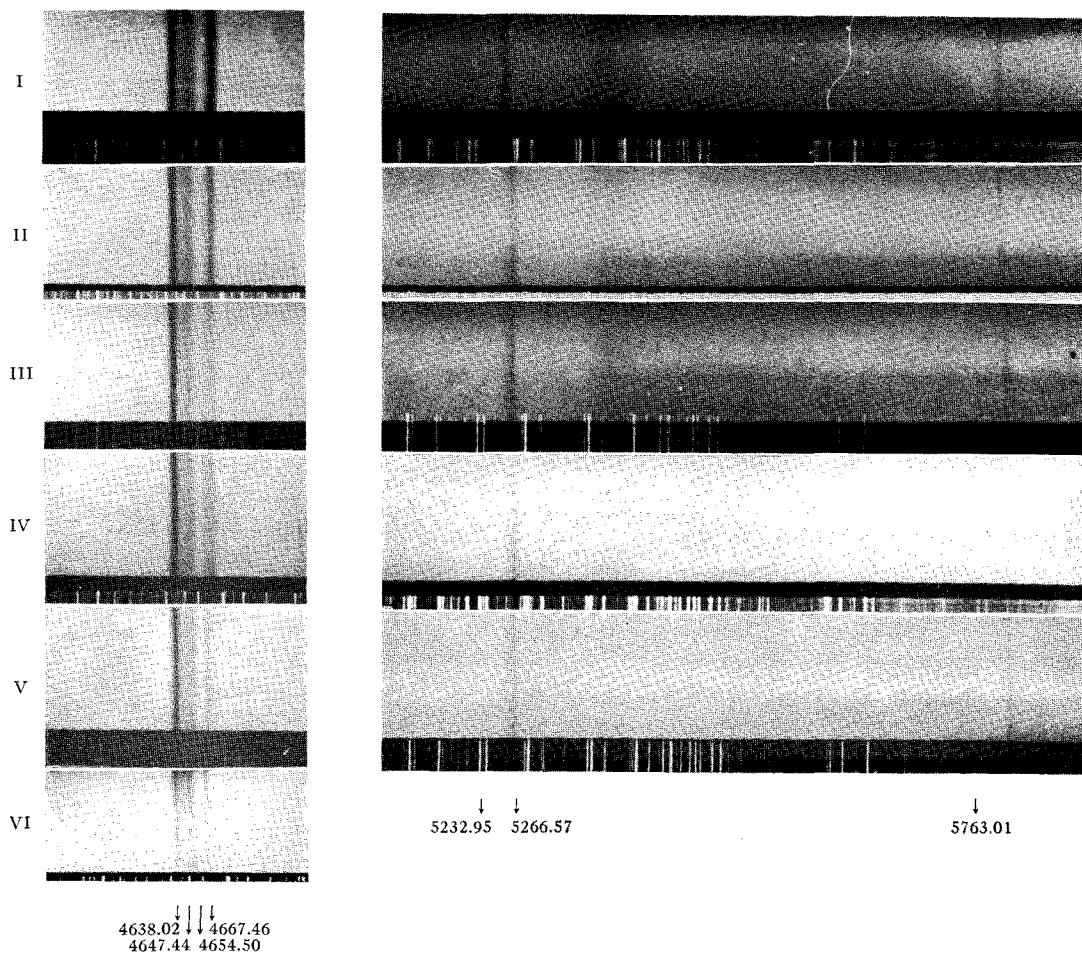


FIG. 2. 0.0012 mole europium chloride in 60 cc anhydrous alcohol to which were added the following amounts of water; I, 0.0 cc; II, 0.16 cc; III, 0.30 cc; IV, 0.45 cc; V, 0.62 cc; VI, solution contains 10 percent water.

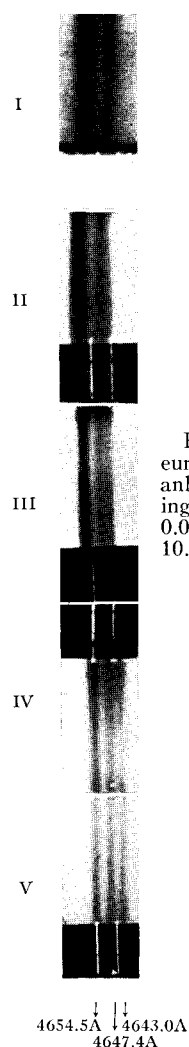


FIG. 3. Concentrated solution of europium nitrate (0.001 mole) in 60 cc anhydrous alcohol to which the following amounts of water were added; I, 0.0 cc; II, 0.87 cc; III, 4.03 cc; IV, 10.06 cc; V, 19.88 cc.

little by little to the solution of the nitrate in ether? It was in response to the same sort of question that potassium nitrate was added to a solution of europium chloride. The situations we are to describe consist of anhydrous europium chloride in absolute alcohol to which water is added in increasing portions and anhydrous europium nitrate in the same mixed solvent.

Anhydrous europium chloride was prepared under conditions suggested by Dr. G. P. Baxter of Harvard University. The hexahydrate was heated in a stream of dry hydrogen chloride between 130°C and 140°C. The released water vapor which condensed on the cooler parts of the glass apparatus was pumped out of the system after the temperature of the furnace had been lowered to room temperature. A stream of dry hydrogen chloride was then passed over the salt again and the temperature was raised back to 130°C–140°C. This cycle was repeated until no

further mist could be seen to collect on the glass. According to Dr. Baxter, dehydration carried out at 130°C results in about 0.1 percent or less moisture in the chloride.

The ethyl alcohol used to dissolve the chloride was prepared by dehydrating 95-percent ethyl alcohol over anhydrous calcium sulfate ("drierite").<sup>7</sup> The dried alcohol after distillation had a refractive index  $n_D^{25}$  1.35944 which according to the *International Critical Tables* corresponds to a purity of 99.93 percent  $\pm 0.06$  percent. We never succeeded in obtaining alcohol of this purity again by this method. With magnesium ethylate, however,<sup>8</sup> this purity was easily achieved. Commercial absolute alcohol was refluxed over the magnesium ethylate and then distilled in an all-glass apparatus. Alcohol dried in this way had a refractive index identical with that dried with "drierite" but another attempt led to a refractive index  $n_D^{25}$  1.35939 or a purity of 100.05 percent  $\pm 0.06$  percent according to the values in the *International Critical Tables*.

The dilute europium nitrate solution was made by dissolving 0.077 g europium nitrate in 40 cc of alcohol 99.93 percent pure to which 20 cc of the purest alcohol was added.

The anhydrous europium nitrate was obtained by dehydrating the hexahydrate under two sets of conditions, one recommended by Dr. B. S. Hopkins of the University

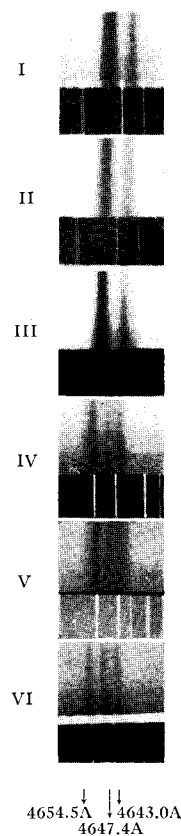


FIG. 4. Dilute solution of europium nitrate (0.0012 mole) in 60 cc anhydrous alcohol to which the following amounts of water were added; I, 0.0 cc; II, 0.02 cc; III, 1.01 cc; IV, 10.68 cc; V, 12.88 cc; VI, 15.88 cc.

<sup>7</sup> W. A. Hammond and J. R. Withrow, *J. Ind. and Eng. Chem.* **25**, 1112 (1933).

<sup>8</sup> H. Lund and J. Bjerrum, *Ber.* **64B**, 210, (1931).

of Illinois which consisted in heating at 90°C for four days in a vacuum line at a final pressure of about  $10^{-5}$  mm Hg. The other procedure due to Dr. P. Selwood of Northwestern University was to heat the hydrate at 200° to 220°C for about three hours in a high vacuum. First the nitrate was heated for several hours at 130°C. Then the lumps of solid were powdered by grinding with a glass rod. Finally the temperature was raised to 200°C–220°C. It was found in a test that the products resulting from both methods had the same spectra and thereafter the shorter method was employed.

The spectrum of the anhydrous chloride in 99.93-percent alcohol consisted of a triplet in the region 4650Å with wave-lengths 4641Å; 4650Å (rather diffuse) and 4662.5Å. This triplet is reproduced in Fig. 2. In the green was a rather fuzzy doublet about 6Å wide over-all with center at 5260Å, at 5340Å a faint diffuse band about 40Å wide, and in the yellow two sharp lines very close together, the more intense component at 5795Å. To 65 cc of the alcoholic solution which contained 0.28 g  $\text{EuCl}_3$  0.09 cc water was added. (The absorption tube was about 90 cm long). A considerable drop in the intensity of the absorption was noted at once and this decrease continued with further additions of water. A faint new line appeared at 4658Å. The faint line in the yellow also increased in strength relative to its neighbor. Indeed its strength seemed to come at the expense of the neighboring line. The lines at 4641Å and 4650Å showed little change in their intensities. The conclusion to be drawn is that these two lines represent the superposition of the lines of the alcoholate and of the hydrate and that the relative sums of the intensities change but little as the transformation of the alcoholate into the hydrate takes place. The isolated lines of these forms at 4658Å (hydrate) and 4661Å (alcoholate) change a great deal in their intensities. Upon adding more water the line which had been rather diffuse at 4650.0Å became sharper and a new line at 4645.5Å appeared. When the solution contained about 10 percent water the alcoholate line at 4661Å had completely disappeared. The chloride-quartet of the aqueous solution was now unmistakably present alone and further dilution merely confirmed its presence.

Changes in the green and in the yellow regions of the spectrum also accompanied the change in

the solvent. New lines set in at 5251Å and 5255Å besides the strong line at 5258Å. In 99.93-percent alcohol the rather fuzzy structure had appeared on the long wave-length side of the stronger line. The faint line in the yellow region became stronger with increased amounts of water and its companion weaker. Finally the latter disappeared. The presence of the original faint line in the alcohol spectrum must be ascribed to the water still present in the alcohol. That this inference is correct is confirmed by the absence of this component when the nitrate was dissolved in a dryer alcohol, and its emergence in the spectrum of the nitrate when water was added. In the spectra of the chloride, no perceptible shift occurred in the lines of the spectrum as the nature of the solvent was altered. In a strict sense, the combined spectrum in the alcohol-water mixtures may be taken as the superposition of the spectrum of the chloride in pure alcohol and of the spectrum of the chloride in pure water. Only the relative amounts of the separate forms changed.

The spectrum of europium nitrate showed variation as the composition of the solvent was changed. In 99.96-percent alcohol (a mixture of the two preparations of alcohol previously described) the spectrum at 4650Å was made up of three lines having but little resemblance to the nitrate-triplet. The lines of the latter were almost of equal intensity and the intervals were roughly equal. The triplet from alcohol had two of their lines so close together that the group might have been taken for a doublet had not a resolution been obtained from a more dilute solution.<sup>9</sup> In alcohol the salt possessed lines at 4650.3Å; 4658.6Å; and at 4660.7Å. There was a very faint line at 4648.1Å which gained in strength when water was added and hence it owed its origin to the water still left in the alcohol. As this line became stronger, the line at 4660.7Å became weaker but persisted to a rather high concentration of water. It could no

<sup>9</sup> When the nitrate was dissolved in ether (reference 1) a doublet appeared in this region of the spectrum. We have then the progression—an evenly spaced triplet from water, a triplet with two of the lines close together from alcohol, and a doublet (a fusion of the two lines?) from ether. This behavior is in agreement with the idea that with greater polarity of the solvent, the energy levels of the dissolved ions are decomposed to a greater degree and that in less polar solvents the fields acting upon the dissolved ions are more symmetrical.

longer be detected when the solution contained 20 percent water.

In the green region of the spectrum the lines were rather diffuse and difficult to characterize. In the yellow, only one line occurred in the spectrum of the nitrate in the alcohol. However, a second one appeared next to it immediately as water was added and the strong line originally present weakened and finally disappeared.

As with the chloride, the intensity of the absorption was greatly decreased when dilution with water took place. The spectrum of the nitrate became especially diffuse when about 4.5 cc of water had been added. The lines sharpened however, as the content in water was further increased. Another sign of interaction of the "pure forms" was brought out by the shifting of the lines as dilution progressed. No such behavior had been observed in the spectra of the chloride. However, it was possible, by following the shift as dilution proceeded, to identify the lines by the positions they assumed when the only remaining spectrum was that of the hydrate. This spectrum was present alone when the water composed 25 percent of the solvent.

The movement of the lines can be observed on Fig. 3 and Fig. 4 by comparing with the adjacent emission spectrum of the iron arc. For example, the line of the hydrate which was barely visible in alcohol had a wave-length of 4647.5Å but when the solution consisted of 25 percent water the wave-length was 4645.0Å. Whether there existed any discontinuities in the shifts of these lines as a function of the amount

of water added we are unable to state at present. The shift appeared gradual within the errors of measurement. Nevertheless, the lines remained sharp, not spreading over the intervals through which the lines were displaced. The sharpness of the lines rules out the possibility that they were a blend between their initial and final positions, that is, between the spectra of the salt in absolute alcohol and in pure water.

It has already been observed<sup>10</sup> that the rather diffuse spectra of the salts of neodymium and of praseodymium showed differences when the salts were dissolved in water and in alcohol and that differences persisted in the mixed solvent.

It has become the practice in some experiments involving the inter-ionic attraction theory to synthesize a solvent of a given dielectric constant by mixing various substances. In the light of the spectroscopic results, it is to be observed that the components of the solvent are singled out by the ions and they take part in different configurations of the electrical fields about the ions. To some degree these ions possess different properties. However, if the behavior of europium nitrate is taken as a guide, it would seem that each configuration is affected in a continuous manner as the solvent is gradually changed. That is, a given configuration seems to respond rather sharply to some average in the macroscopic properties of the pure solvents.

This work is greatly indebted to the Penrose Fund of the American Philosophical Society.

<sup>10</sup> H. C. Jones and J. A. Anderson, *The Absorption Spectra of Solutions* (Carnegie Institution of Washington, 1909), pp. 79, 95.