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Citation: *The Journal of Chemical Physics* **18**, 789 (1950); doi: 10.1063/1.1747776

View online: <http://dx.doi.org/10.1063/1.1747776>

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Variations in Absorption Spectrum of the Nitrate Group

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(Received February 24, 1950)

Lithium, magnesium, calcium, aluminum, manganous, cobaltous, nickelous, cupric, zinc, cadmium and thorium nitrates, and nitric acid, show an absorption in tertiary butyl alcohol solution which is different from that of dilute aqueous solutions of nitrates. The most marked effects are shown by the transition elements with partially completed *d* shells. The variety of the spectra indicate that a single change, such as the rearrangement of the normally planar nitrate ion into a pyramidal form, cannot account for nitrate spectrum changes.

DILUTE aqueous solutions of nitrates show a similar absorption in the ultraviolet which is attributable to the nitrate ion. There is a rounded peak at 300 millimicrons with a molal extinction coefficient approximating 7, and a sharply rising "end-absorption" as one progresses to shorter wave-lengths from about 265 millimicrons. The behavior of this peak under a number of conditions was studied by Schaefer.¹ The conclusion drawn was that the spectrum is a characteristic of the nitrate ion, whether in aqueous solution or in a melt of the solid.

Some salts show variations from Beer's Law under conditions of high concentration in water, or when alcohol is present in high concentrations. In the early days of absorption spectroscopy it was customary to attribute such deviations to "physical" influences in the environment of the absorbing entity. Schaefer² championed the view that every deviation from Beer's Law rests in chemical rather than physical alterations. For the case of the nitrate group, he showed that the absorption of 98.6 percent nitric acid, ethyl nitrate, and nitric acid in ethyl ether resemble each other, and are different from that of nitrate ion. This paper was followed by systematic studies of a number of salts, mostly nitrates.³

A summary by von Halban,⁴ discussing data in publications by himself, Ebert, and Eisenbrand, reviewed the alterations of the nitrate ion spectrum in aqueous solution as a function of salt concentration. He pointed out the specific nature of the cation effects in the concentrated solutions, driving the absorption peak to higher extinction and lower wave-length values, and that the alterations could be shown not to be due to formation of nitric acid. In the specific case of nitric acid, he pointed out that the spectrum in concentrated acid was neither the spectrum of the nitrate ion, nor that of nitric acid in hexane, in which a spectrum similar to that of nitrate esters was found. Besides bringing in the factor of ionic deformability in explaining the results with the various salts, he pointed out the transition nitrate ion-hydronium nitrate-HNO₃ involved in the

series of nitric acid spectra, and the applicability of similar stages to the spectra of the other nitrates.

Kortüm,⁵ from similar studies of nitrate absorption in concentrated salt solutions, also pointed out the possibility of a water-anion interaction in the coordination sphere of a cation in concentrated aqueous solution. He voiced the further possibility that a change in the shape of the normally planar nitrate ion might be involved. Holleck⁶ interpreted the phenomenon of catalysis of nitrate reduction at the dropping mercury electrode through polyvalent cations such as lanthanum as due to a change in shape of the planar nitrate group to the chemically less stable pyramidal form, citing the optical findings of von Halban and co-workers as evidence for this change in shape. From his reduction results, Holleck estimated the degree of transformation to the pyramidal form to be of the order of 95 percent for solutions in water 0.1*N* in lanthanum chloride.

Studies in this laboratory of the absorption of cobaltous nitrate dissolved in tertiary butyl alcohol⁷ have shown a characteristic change in the nitrate absorption which far exceeds the difference between the spectra of nitrate ion and HNO₃. The absorption is shifted to shorter wave-lengths, the peak coming at about 285 millimicrons, and the molal extinction coefficient at this wave-length is about 112. A survey was therefore made of the absorption spectra of a number of nitrates soluble in tertiary butyl alcohol. Curves are shown in Fig. 1 for lithium, magnesium, calcium, aluminum, manganous, cobaltous, nickelous, cupric, zinc, cadmium, and thorium nitrates, and nitric acid, in tertiary butyl alcohol. There is also a reference curve of lithium nitrate in 50 percent tertiary butyl alcohol (lithium or other nitrate in dilute water solution is indistinguishable). The logarithm of the formal extinction coefficient (calculated per nitrate) is plotted against the wave-length to facilitate comparison of the curves even with large differences in extinction coefficient. The curves have been corrected for the absorption of solvent and of cation, the latter being significant only for the cupric case. The curves plotted are representa-

¹ K. Schaefer, *Zeits. f. wiss. Phot.* **8**, 212-234 (1910).

² K. Schaefer, *Zeits. allgem. anorg. Chemie* **97**, 285-311 (1916).

³ K. Schaefer, *Zeits. wiss. Phot.* **17**, 193-217 (1918).

⁴ H. von Halban, *Zeits. Elektrochemie* **34**, 489-497 (1928).

⁵ G. Kortüm, *Zeits. Elektrochemie* **50**, 144-149 (1944).

⁶ L. Holleck, *Zeits. f. physik. Chemie* **194**, 140-169 (1944).

⁷ L. I. Katzin and E. Gebert, *J. Am. Chem. Soc.* (to be published).

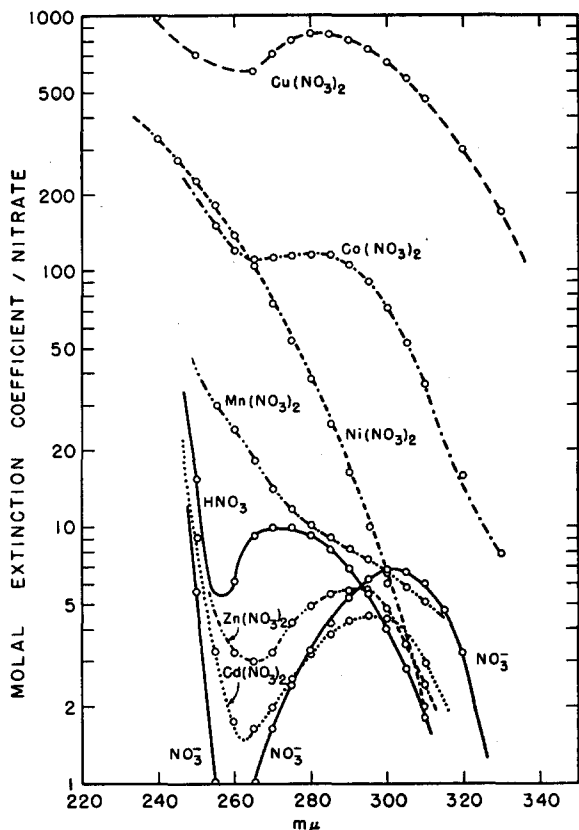


FIG. 1a.

tive members chosen from several runs, and the extinction coefficients at a given wave-length are good to at least 2 percent. The relations of points on a given curve are much more exact than this.

The striking feature of Fig. 1 is that all of the absorption curves for nitrate salts in tertiary butyl alcohol differ markedly from that of free nitrate ion. Furthermore, the spectra cannot be attributed to a mixture of the spectra of nitrate ion and nitric acid. A whole series of nitrates shows spectra more intensely absorbing than that of nitric acid, at the wave-length of its peak (270–275 millimicrons). These nitrates are the transition element nitrates: manganous, cobaltous, nickelous and cupric; and thorium nitrate.

From these observations it is seen that there exists a large range of spectral changes which can be induced in the absorption of the nitrate group. It therefore seems clear that one cannot follow Holleck⁶ in ascribing the relatively minor spectral changes found in aqueous solution to changes in configuration of the nitrate group from planar to pyramidal. To ascribe the spectral alterations to ion shape changes would necessitate as many shapes as there are spectra. It therefore seems reasonable to consider the spectral alterations to be due entirely to shifts in electron orbits without alteration of the planar distribution of the atoms.

It seems significant that the most marked changes are found for the nitrates of the transition elements whose

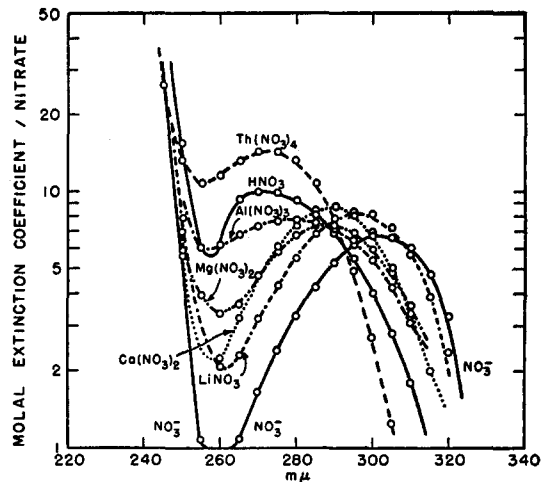


FIG. 1b.

ions contain partially completed shells of outer electrons. This is true for the manganous, cobaltous, nickelous and cupric nitrates. Zinc and cadmium are also transition elements, but the zinc ion has full orbitals through the 3*d* shell, and cadmium has full orbitals through the 4*d* shell. The spectral effects for the nitrates of these metals are very small. In addition, both of these ions have colorless solutions. Manganous, cobaltous, nickelous and cupric solutions are colored, and the last three at least show a noticeable difference in color between the aqueous and tertiary butyl alcohol solutions of the nitrates.

The simple charged ions of the other metals tested in these investigations—lithium, magnesium, aluminum, calcium, and thorium—all possess noble gas configurations, with completed electron shells. One may postulate for these (including hydrogen ion) that the effect on the nitrate spectrum is a function of electrostatic charge and effective ionic radius. Thus, hydrogen, with the smallest ionic radius, and thorium, with the greatest ionic charge, show the largest effects on the nitrate ion spectrum. The zinc and cadmium salts, because of the completed shells, might also be considered with this group.

It has been shown in the case of cobaltous nitrate that there is complex formation between the metal atom and the nitrate groups.⁷ In the cases of nickelous and cupric ions, addition of a small proportion of lithium nitrate to the metal perchlorate solutions in alcohol gives essentially the same spectrum as is shown by the bivalent metal nitrate solution alone, in complete parallel to the behavior of the cobalt case. In the case of the manganous salt, the only spectral data are for the addition of lithium nitrate to manganous perchlorate solution, since the solid manganous nitrate is unavailable commercially. The difference of the spectrum from that of lithium nitrate in tertiary butyl alcohol is evidence that nitrate has been transferred

to the manganous atom, although the completeness of the transfer cannot be assessed. Evidence from the cobalt nitrate studies has shown that lithium nitrate in tertiary butyl alcohol is essentially completely non-dissociated, so that the proportion of transfer is a measure of relative firmness of binding of the nitrate group to the metal atom. These data serve to confirm the suggestion of Kortüm⁵ and that implied in the earlier work of von Halban and co-workers,⁴ that co-ordinative binding of the anion may be the influence in the spectral changes found in concentrated nitrate solutions.

For the case of nitric acid in dioxane solution, von Halban and Litmanowitsch⁸ showed unmistakably individual spectra for HNO_3 , H_3ONO_3 (hydronium nitrate) and nitrate ion. Similar findings have been made for other absorbing anions such as picrate,⁹ with the tendency for the spectra of the free anion and the electrostatically associated hydronium acid to be quite similar. A parallel type of absorption change has been found for both the cobalt and the nitrate groups in cobaltous nitrate in organic solvents.⁷ Semiquantitatively similar color changes of the cupric and nickelous nitrate solutions, as well as the change in the absorption

of lithium nitrate with water content of the tertiary butyl alcohol solution, indicate the phenomenon is probably general.

EXPERIMENTAL

A model DU Beckman quartz prism spectrophotometer was used. The hydrated nitrates were dissolved in anhydrous tertiary butyl alcohol. In most cases the concentration of the stock solution was checked by analysis. In some cases a water analysis of the solid starting material served to give the hydration correction. The copper nitrate was made up in tertiary butyl alcohol containing about half its concentration of nitric acid, to avoid solution instability which was occasionally manifested in the absence of this precaution. The acidified alcohol was also used for the aluminum nitrate solution. In some experiments, perchlorate solutions were used, and a small proportion of lithium nitrate added. In the case of cobalt, copper and nickel solutions, the spectra thus obtained were essentially identical to those made by dissolving the nitrate salt. In the case of the manganous solution, the solid nitrate was not available, so only the perchlorate-nitrate curve was used. In all cases, blanks were properly made up to give correction for added nitric acid or metal perchlorate. The latter was significant only for the case of copper.

Grateful acknowledgment is made of the technical assistance of Miss Elizabeth Gebert.

⁸ H. von Halban and M. Litmanowitsch, *Helv. Chim. Acta* **31**, 1963-71 (1948).

⁹ F. Bortini, *Zeits. f. physik. Chemie* **87**, 104-115 (1914).

Statistical Mechanics of Adsorption. X. Thermodynamics of Adsorption on an Elastic Adsorbent

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(Received February 2, 1950)

Thermodynamic equations are derived which should be useful in the analysis of experimental data and theoretical models referring to the adsorption of a one-component gas on an elastic adsorbent. This problem is closely related to the thermodynamics of adsorption of a solute from a liquid solution onto an elastic adsorbent immersed in the solution (e.g., a myosin thread).

I. INTRODUCTION

STUDIES on (a) the adsorption of gases by rubber, textiles, proteins and other elastomers *not* under tension and on (b) the effect of the presence of a gas (constant pressure) on the length-tension curve of certain elastomers are, of course, well known. An obvious extension of this work is to measure adsorption isotherms with the adsorbent under tension. Such measurements should, for example, contribute to our knowledge of how the structure of certain proteins changes with extension.

The author is unaware of published investigations of this type. In anticipation of future experimental and theoretical efforts in this direction, we attempt here a brief thermodynamic analysis of the problem. The

methods are essentially those of paper IX¹ of this series; we omit the straightforward extension to adsorption from a mixture of gases.¹

Aside from intrinsic interest, gas adsorption is, of course, closely related thermodynamically to adsorption from a liquid solution, so that many equations given here will be approximately valid for a solution, replacing gas pressure by concentration or activity of the solute. There have been recent suggestions²⁻⁵ that muscular contraction may involve "adsorption" of ions from solu-

¹ T. L. Hill, *J. Chem. Phys.* **18**, 246 (1950).

² J. Riseman and J. G. Kirkwood, *J. Am. Chem. Soc.* **70**, 2820 (1948), and references contained therein.

³ A. Katchalsky, *Experientia* **5**, 319 (1949).

⁴ W. Kuhn, *Experientia* **5**, 318 (1949).

⁵ J. Botts and M. F. Morales (in preparation).