A Raman Investigation of the Possible Existence of Certain Inorganic Complexes in Solution

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This investigation was undertaken for the purpose of establishing the possible existence of certain inorganic complexes in solution. Their existence or non-existence would answer the question raised by Freed and Kasper[2] with respect to the interpretation given by McBain and Van Rysselberge[3] to electrical transference data.

With the object of obtaining evidence supporting one or the other of these views, a Raman investigation has been made with solutions of ammonium sulfate, of manganese sulfate, and of mixtures of these, in the hope of finding a new line or lines characteristic of complexes.

Experimental

The apparatus used for obtaining the spectra has been described previously.[4] The investigation was undertaken after it was found that the great brilliance of the arc gave promise of easily detecting complexes which should give very weak lines by ordinary means of excitation.

Saturated solutions were prepared of recrystallized manganese sulfate and of ammonium sulfate. Two mixtures were made of these solutions. The first contained one part of the saturated solution of manganese sulfate, one part of the solution of ammonium sulfate and two parts of water. The second mixture was 2 M ammonium sulfate and 0.05 M manganese sulfate. The water used was distilled from phosphoric acid as recommended by Ellis and Kiehl[5]; this procedure eliminated the generalized fogging of the photographic plate obtained with water distilled from alkaline permanganate. In all cases the solutions were at 60°.

The data obtained are given in Table I. The lines are accurate to one Ångström. The wave number differences are inscribed with s, m and w, which represents a visual estimate of the intensities as strong, medium or weak, while the letter b signifies a band.

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(2) Freed and Kasper, THIS JOURNAL, **52**, 2632 (1930).
(3) McBain and Van Rysselberge, *ibid.*, **52**, 2336 (1930).
(4) Houlton and Tartar, *ibid.*, **60**, 544 (1938).
(5) Ellis and Kiehl, *ibid.*, **57**, 2145 (1935).

TABLE I

RAMAN SHIFTS FOR THE DETERMINATION OF POSSIBLE COMPLEXES

Substance	Concn.	Raman shifts
Water	Pure	441–914mb, 1650mb, 3176–3640sb
$(NH_4)_2SO_4$	5.8 M	447m, 613m, 791w, 981s, 1029–1139mb, 1425m. 2832w
$MnSO_4$	3.3 M	447m, 603w, 981s, 1120mb

Discussion and Conclusions

In the two mixtures only the line 791 cm.$^{-1}$ failed to appear; all others were present. No new lines characteristic of a complex formation were observed. This non-appearance of Raman radiation under exceptionally intense illumination confirms the findings of Freed and Kasper[2] from the determination of magnetic susceptibilities and practically disposes of the notion that complexes, predominantly homopolar in character, exist in appreciable quantity in the solutions. Certainly, such complexes do not exist to the extent indicated by McBain and Van Rysselberge[3] to account for their transference data using similar systems.

The 791 cm.$^{-1}$ and 2832 cm.$^{-1}$ of the ammonium sulfate and the active frequency shift 1120 cm.$^{-1}$ of manganous sulfate have not been previously reported.

The average fundamental frequency shifts 447, 613, 981, 1117 cm.$^{-1}$ may be attributed to the sulfate ion. The higher frequency shifts are attributed to the ammonium ion. The diffuse character of the band 1029–1139 with its maximum intensity at 1115 may be due to the overlapping of the frequency shift of the sulfate ion with that of the ammonium ion, both occurring at approximately 1100 cm.$^{-1}$. The line showing a frequency shift of 2832 is probably due to the ammonium ion. That this line could not be excited by the 4916 mercury line is apparent, for this would lead to a frequency shift of 200 cm.$^{-1}$ which makes its existence improbable. It should be mentioned that at approximately 6500 Ångströms there appeared a broad band when the manganous sulfate solution was used. This band could not be attributed to other

exciting lines and has not been included in Table I.

The effect of electrolytes on the bands of water was noticeable. The band at 700 cm.$^{-1}$ tends to decrease in intensity, that at 1650 cm.$^{-1}$ remains practically constant in intensity, while that at 3433 cm.$^{-1}$ increases. Finally the manganese sulfate solution brought out another band at 7500 cm.$^{-1}$.

Summary

A Raman investigation of the possible existence of certain complexes in aqueous solutions of ammonium sulfate and manganese sulfate has been made with negative results. Several new lines were found for manganese sulfate and ammonium sulfate solutions.

Ternary Systems. XXII. Formation of Solid Solutions from Alums

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Since the introduction of the idea of isomorphism into chemical thought by Mitscherlich,[2] the clarification of that concept has not proceeded as rapidly as might have been wished. Originally conceived somewhat vaguely perhaps as a condition of simultaneous crystallization of crystallographically similar bodies, isomorphism was recognized much later by van't Hoff[3] as a condition of solid solution, though the allocution "mixed crystals" still remains in general usage to confuse thought. Experimental work has differentiated cases of unlimited mutual solubility from cases of limited mutual solubility, and Roozeboom[4] has discussed the five classes which are commonly met with, based upon the ratio of components in the liquid and in the solid phases; to these Ricci[5] recently has suggested that a sixth class might well be added. Since the time of the application of X-ray methods to the determination of structure of solids, much has been learned with regard to the structure of solid solutions.

With respect to the relations of solid solutions to liquid solutions, although there has been a considerable amount of painstaking work, nevertheless, the total is not impressive as representing a century of effort. Not only is the quantity of this work not very large, but some fractions of it are not suitable for quantitative use because no criteria have been applied as to the existence of a true state of equilibrium in the solid phase. The present paper and others which are to follow are intended to present results in which there may be confidence as to the attainment of equilibrium with the hope that they may contribute reliable data toward the eventual moulding of a theory of solid solutions.

The alums constitute a class in which isomorphism was recognized by Mitscherlich; as far as they have been investigated, it appears that they are in most cases mutually soluble in all proportions. Of the four alums used in this investigation, three have been studied previously as to their formation from their component salts. We have included a study of the formation of the fourth of these, the ammonium aluminum alum, together with the mutual relations of three pairs of alums. Brief statements will be made as to the analytical methods used in each case; the following general statements apply to all the experiments. The work was conducted at 25 $\pm$ 0.03°, in small glass-stoppered tubes, containing about 50 g. of material. The original complexes were weighed into the tube, using materials chosen so that their composition could be relied upon to give a fixed point upon the tie-lines to be used in determining composition of solid phases by extrapolation. In order to establish that the solid solutions had reached equilibrium, duplicate complexes were made up for each experiment, but in different order of addition; in one tube the first solid component was dissolved in the water completely and the second solid then added, while in the second tube the order was reversed, thus ensuring that the final solid had been formed from the two different pure components in the two

(1) This paper is an abbreviation of the thesis presented by Mr. Kaplan in partial fulfilment of requirements for the Ph.D. degree at New York University, June, 1936.

(2) Mitscherlich, Berl. Akad. Abhand., 426 (1818–1819); Ann. chim. phys., 14, 72 (1820); 19, 350 (1821).

(3) Van't Hoff, Z. physik. Chem., 5, 323 (1891).

(4) Roozeboom, ibid., 8, 504 (1891).

(5) Ricci, THIS JOURNAL, 57, 805 (1935).