Chemical Applications of the Raman Effect: II. Common Ion Effect

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In view of these facts, therefore, it is not surprising that methyl methacrylate monomer possesses a frequency at $\Delta\tilde{\nu}$ 3100 corresponding to the linear oscillation of the hydrogen atoms attached to the ethylenic group and an additional frequency at $\Delta\tilde{\nu}$ 3005, likewise attributable to the movement of hydrogen atoms. In the completely polymerized product, on the other hand, the large shift at $\Delta\tilde{\nu}$ 3100 is completely absent. The only reasonable explanation of this disappearance is found in the absence of the $=CH_2$ group. This is additional evidence of the breakdown of the ethylenic linkage and the formation of a chain through the end carbon atom.

Up to this point little has been said in regard to the spectrum shown in Fig. 2 for partially polymerized methyl methacrylate. This spectrum, as is apparent, is practically identical with that of the unpolymerized monomer. The solutions in these experiments with the partially polymerized product were varied over a wide range of viscosities from a value approximating that of glycerine to a solution so highly viscous that no flow was observed in a period of 24 hours under a pressure corresponding to several centimeters of the liquid. The actual viscosity is of little importance. The essential fact is that, after increasing the viscosity until it has reached a value many thousand times its initial amount the spectrum remains largely unchanged. These observations are susceptible of but one interpretation. A small amount of polymerization has an enormous effect on the viscosity. Any concentration of the polymer in excess of 5 percent to 10 percent would have been detectable. In the absence of such indication, less than this amount of polymerization must produce the marked alteration in physical properties.

The microphotometer used to trace the photographic plates is a two-speed Kipp and Zonen type A Moll instrument. The spectrograph used in these experiments is the Gaertner model L 230 having a single glass prism with a camera lens having an effective aperture of F 16. The dispersion on the photographic plates at λ4358 was 35A per millimeter. The wave-lengths of the Raman lines were determined by interpolation from the nearest iron arc lines.

Chemical Applications of the Raman Effect: II. Common Ion Effect

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It has been shown by means of the Raman effect that the ionization of homopolar compounds in dilute solution increases more rapidly than is proportional to the dilution. This ionization will be repressed by adding a common ion and such repression is proportional to the concentration of the common ion added. In mixtures of two compounds, both being homopolar and containing a common cation, there is little effect on the ionization. On the addition of a neutral salt containing an anion which may be shared with a cation already combined in homopolar linkage with another anion the equilibrium resulting is in the direction of the formation of that compound whose linkage is the most homopolar. These results indicated by means of the Raman effect cannot be observed with equal facility by any other method of approach.

THE influence of adding common ions to solutions of compounds whose anions are bound by a linkage homopolar in nature is investigated by means of the Raman effect. This is possibly the only practical method for investigating solutions of this type. While the results are in more or less agreement with what may be expected from the classical theory of the common ion effect, there has heretofore been no extensive means available which would permit such a correlation.

The Raman spectra of aqueous solutions of zinc chloride and its combinations with alcohol have been previously investigated by Hibben.[1,2]

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[1] Hibben, Proc. Nat. Acad. Sci. **18**, 532 (1932).
[2] Hibben, Phys. Rev. **51**, 593 (1937).

The aqueous solution gives rise to at least one line corresponding to the Zn←→Cl (v_r) oscillation of 275 wave numbers per centimeter. In concentrated solutions its intensity indicates a strong homopolar linkage. In the more dilute solutions there is a diminution of the intensity with increased ionization. Consequently any suppression of ionization will increase the intensity of this line as Zn^{++} and Cl$^-$ are incapable of giving rise to any Raman effect.

From the classical theory of the common ion effect, the addition of the Cl ions should be in the direction of repressing ionization and consequently increasing the intensity of the Raman line corresponding to the Zn←→Cl vibration. However, such observations as have been made heretofore were either on dilute solutions or solutions in equilibrium with two phases. These experiments indicate that there is a repression of ionization on the addition of a common ion in both dilute and concentrated solutions, even though the solution may be apparently homogeneous, and in the complete absence of a two-phase equilibrium. In addition to these effects there is indicated, in the case of zinc chloride solutions, a greater increase in ionization on dilution than is proportional to the amount of dilution. These results are indicated in Fig. 1.

Beginning with a 1 molal zinc chloride solution the concentration is decreased to one-half, at which point, as is illustrated in curve 2, the intensity of the Zn – Cl shift is not diminished to one-half but to nearly zero, which indicates that in a half molal ZnCl$_2$ solution there is practically complete ionization. But on the contrary in a solution of a $\frac{1}{4}$ molal zinc chloride and 1 molal sodium chloride, there is some evidence for the reappearance of the Zn – Cl shift. Keeping the zinc chloride concentration to $\frac{1}{4}$ molal, but increasing the sodium chloride to 2 molal, enhances the intensity of the Zn – Cl line so that it is nearly one-half the value noted in the original 1 molal solution of zinc chloride. With $\frac{1}{2}$ molal zinc chloride solution, 2 molal with respect to sodium chloride, the intensity is even greater than with the 1 molal solution. This would indicate that the 1 molal solution of zinc chloride was at least 50 percent ionized, and that such ionization will be increased with the dilution to an exceptional degree. This may be repressed by the

addition of the common chlorine ion, such repression being roughly proportional to the concentration of such an ion. There seems to be, however, a minimum effectivity since the production of free chlorine ions from the ionization
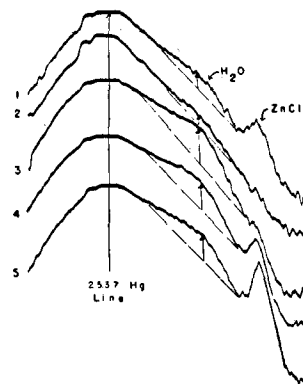

FIG. 1. Microphotometer tracings of the Raman spectra from zinc chloride solutions of the following compositions: curve 1, 1 molal zinc chloride; curve 2, $\frac{1}{2}$ molal zinc chloride; curve 3, $\frac{1}{4}$ molal zinc chloride 1 molal sodium chloride; curve 4, $\frac{1}{4}$ molal zinc chloride 2 molal sodium chloride; curve 5, $\frac{1}{2}$ molal zinc chloride 2 molal sodium chloride.

of the zinc chloride alone in passing from 1 molal to $\frac{1}{2}$ molal solution is insufficient to accomplish this effect.

In these solutions there is also a concomitant effect upon the water band occurring near $\Delta\bar{\nu}$ 150–170 attributed to the hindered translational motion of the water molecules. This is apparently enhanced by the sodium chloride and is diminished by small quantities of zinc chloride.

The next logical procedure would be to ascertain the effect of adding a common zinc ion. For this purpose zinc sulfate was chosen. This gives rise to at least four frequencies, $\Delta\bar{\nu}$ 448, 614, 980 and 1105. These are in reasonable agreement with similar frequencies observed in other sulfates. There is some evidence of a frequency slightly less than $\Delta\bar{\nu}$ 448 which is broad and diffuse. These results are shown in Fig. 2, in which curve 1 represents a 1 molal solution of zinc sulfate, and curve 2, a 1 molal zinc chloride solution. The line occurring in close proximity to $\Delta\bar{\nu}$ 614 is the 2576A mercury line. Curve 3 represents 1 molal zinc sulfate and 1 molal zinc chloride solution from which it is observed that neither the Zn – Cl line nor the SO$_4$ lines are appreciably affected either in intensity or in magnitude of displacement. Curve 4 represents a mixture, the

solution originally having the composition sodium chloride, 4 molal, and zinc sulfate, 2 molal. Finally curve 5 is for a 2 molal sodium chloride and ½ molal zinc chloride solution. From
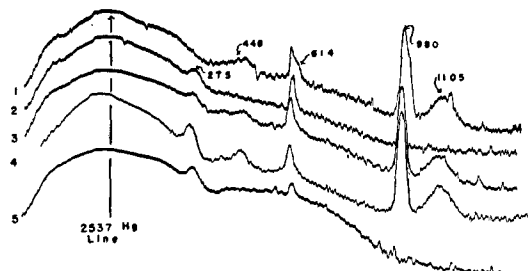

FIG. 2. Microphotometer tracings of the Raman spectra from zinc chloride and zinc sulfate solutions of the following compositions: curve 1, 1 molal zinc sulfate; curve 2, 1 molal zinc chloride; curve 3, 1 molal zinc sulfate 1 molal zinc chloride; curve 4, 4 molal sodium chloride 2 molal zinc sulfate; curve 5, ½ molal zinc chloride 2 molal sodium chloride.

these last two curves it is apparent first that the sodium chloride reacts with some of the zinc sulfate to form zinc chloride but not with all of it. In other words, if the equilibrium were entirely in the direction of formation of zinc chloride and production of sodium sulfate, the line at $\Delta\bar{\nu}$ 275 in curve 4 should have at least twice the intensity it has in curve 3 if the degree of ionization in a 1 molal and 2 molal solution does not differ greatly. This is not quite realized. On the other hand, if there were equal interchange of all ions so as to produce a 2 molal sodium chloride and

1 molal zinc chloride solution, omitting the sulfates from consideration, the $\Delta\bar{\nu}$ 275 line in curve 4 should have approximately twice the intensity it has in curve 5. This also is not realized. Consequently one is led to the conclusion that the equilibrium in such mixtures is slightly in the direction toward the formation of excess zinc chloride. However, in view of the amount of experimental error involved in treating these curves from a strictly quantitative point of view, such a deduction can be considered as only tentative. From curve 3 can be drawn the conclusion that the effect of the zinc ion is not to repress noticeably the ionization of zinc chloride, but to leave the equilibrium relatively undisturbed. This is possibly due to the equal homopolarity of the bonds in either case.

The spectrograph used in these experiments was designed by the author. The optical system consists of two quartz lenses, focal length 24 centimeters, effective aperture F 6.5, each fully corrected for spherical aberration, and one right-hand and one left-hand 60° quartz prism. The dispersion on the photographic plates at λ2537 is 16.5A per millimeter. The microphotometer used to trace the plates is a two-speed Kipp and Zonen type A Moll instrument. The wavelengths of the Raman lines were determined by interpolation from the nearest iron arc lines. The source of excitation was a special model of the Hanovia Sc 2537 silica lamp.

Some Chemical Properties of Element 43

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1. INTRODUCTION

PROFESSOR E. O. LAWRENCE gave us a piece of molybdenum plate which had been bombarded for some months by a strong deuteron beam in the Berkeley cyclotron. The molybdenum has been also irradiated with secondary neutrons which are always generated by the cyclotron. The molybdenum plate shows a strong activity, chiefly due to very slow electrons. The

radioactivity is due to more than one substance of a half-value period of some months and to the radioactive phosphorus isotope P^{32}.[1] The substance was sent from Berkeley on December 17, 1936 and we started our chemical investigation on January 30, 1937; all short period substances have decayed in these 6 weeks and we could

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[1] We will give more details on the radioactive side of this investigation in a later paper to appear in the *Physical Review*.