

LIGHT SCATTERING INVESTIGATIONS OF POLYMOLYBDATES

PART I

DEPOLARIZATION OF LIGHT SCATTERED BY SODIUM MOLYBDATE IN ACID AND BASIC SOLUTIONS

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INTRODUCTION

It is now generally believed that while the molybdate ions exist in the monomeric form in basic solutions, they aggregate to form higher ionic weight species in acid solutions. This aggregation has been extensively studied by Jander (1936) and his co-workers by measuring the diffusion coefficients of polymolybdate ions with decrease in pH . From these observations they have evaluated the ionic weights by using an empirical equation.

An attempt to determine the absolute ionic weights of polymolybdate ions from light scattering measurements has been made by Kestigian and Stein (1953) by using the recent Zimm's (1948) experimental technique. The author along with Katti (1955) has recently investigated the possibility of using the Krishnan (1935) light scattering technique of measuring the depolarization of scattered light by using a pair of double image prisms, for investigating this phenomenon. Preliminary results on the 1.0% solutions of sodium molybdate in the range of pH 8.0 to 0.5 showed the desirability of extending this investigation to sodium molybdate solutions covering a wide range of concentrations, i.e. from very dilute solutions, where the interaction between the ions is negligible to highly concentrated solutions, and to some other molybdate solutions as well, in order to get a better picture of this aggregation and dispersion process. This paper deals with the results on the sodium molybdate solutions in the pH range where no precipitation occurs.

EXPERIMENTAL ARRANGEMENT

A 1,000 watt projector lamp was used as a source of incident light. The rest of the experimental arrangement was similar to that of Krishnan (1935) and need not be described here in detail. The depolarization values ρ_v , ρ_h and ρ_u corresponding to incident vertically, horizontally polarized and unpolarized light respectively were measured by the usual Cornu method using a Nicol on a divided circle.

A blue filter was used in the path of the incident beam. The components H_v and H_H with this arrangement were still very weak—particularly at low concentration, to assure great accuracy in the values of ρ_h . Therefore observations were made for ρ_u and ρ_v in all these cases and the values of ρ_h were calculated from the usual expression $\rho_u = \frac{1+1/\rho_h}{1+1/\rho_v}$ obtained from the reciprocity relation. The values of ρ_h obtained as above were compared with those directly observed with a beam of

sunlight, wherever possible, and have been found to tally well within the range of experimental errors.

PREPARATION OF THE SPECIMEN

Becker's analysed sodium molybdate was used throughout in the present investigations. Solutions of the required concentration were prepared in distilled water and filtered through corning ultra filter glass. The pH of each of the solutions was adjusted by adding the requisite quantity of filtered nitric acid c.p. to the filtered solution. The solutions thus obtained were again filtered several times in the rectangular observation cell till the final specimen used for observations showed no speck of light in a strong beam of convergent sunlight. The amount of nitric acid required to change the pH values in the case of dilute solutions does not appreciably alter the concentration of these solutions. At high concentrations, however, particularly at lower pH values, large quantities of nitric acid have to be added resulting in the change of concentration. The concentration in a 30% solution, for example, reduces nearly to 26% when nitric acid buffer is added to bring it down to 4.0 pH . In order to correct for the buffer concentration effect a separate experiment was performed in which the changes occurring in solutions of various concentrations when nitric acid buffer is added to adjust the pH values at short intervals up to 0.5 were determined. Graphs of resulting concentrations of buffered solutions against their original concentrations for various pH values were plotted. These curves were used to prepare final specimens of the required strength and pH . Both the concentration and the pH were checked before making the depolarization measurements at 35°C. Concentrations were checked from the corresponding refractive indices measured with an Abbey refractometer and the pH measurements were made with a Beckman pH -meter.

DISCUSSION OF THE RESULTS

Observed values of depolarizations ρ_h and ρ_v at different pH ranging from 8.0 to 0.5 at various concentrations are recorded in Tables 1 and 2.

VARIATIONS IN THE SIZE AND SHAPE OF THE PARTICLES AS INDICATED BY THE DEPOLARIZATION VALUES ρ_h AND ρ_v

In general the values of ρ_h in basic solutions at pH 8.0 are in the neighbourhood of 100% indicating ionic sizes ranging from molecular dimensions to about 110 $\mu\mu$. These values remain constant as the pH values are decreased down to 7.0. In the pH range 4.0 to 3.0, ρ_h reach their minimum values indicating the maximum tendency for aggregation in this region. Later on with still further decrease in pH , however, the size of the ionic aggregates becomes smaller and smaller as is shown by the continuous increase in ρ_h .

Variations in ρ_v with pH follow closely those of ρ_h . No change in ρ_v is noticed till the pH decreases from 8.0 to about 7.0. This shows that no change in the shape of the ions or their aggregates takes place in this region. The complete absence of any change in the size and shape of the ions in this region is in agreement with Jander's observations that no change in the ionic weights also takes place in this region. In the pH interval 4.0 to 2.5 where the aggregation tendency is maximum, ρ_v indicates the presence of more symmetric aggregates. This is to be expected if the aggregation is due to rapid symmetric collisions of the type occurring during the earlier stages of precipitation. Below pH 2.5 the values of ρ_v increase gradually with the decrease in the size of the aggregates.

EFFECT OF CONCENTRATION ON THE SIZE AND SHAPE OF THE AGGREGATES

The corresponding values of ρ_h at different concentrations (Table I) show that in the basic solution at 8.0 ρ_h is 100% at all concentrations—from very dilute solutions of about 0.1% to highly concentrated solutions of about 30%. In the pH range in which aggregation occurs, aggregates in concentrated solutions are generally larger than the corresponding ones in dilute solutions. For discussing the changes in ρ_v with concentration in the basic region (8.0 pH) one can divide the concentration range into three broad regions, namely (i) from 0.1% to 0.6%, (ii) 0.8% to 10% and (iii) beyond 15%.

In the first range ρ_v decreases continuously from 4.9% to 2.5%. In the second range the values of ρ_v increase slowly from 3.1% to 13%. Near 15%, however, a sudden rise in ρ_v takes place and we get ρ_v as high as 30%. Later, with further increase in concentration ρ_v slowly decreases again.

The variations in ρ_v thus indicate an appreciable change in the shape of the particles with concentration. Even at very high dilutions the ions show a finite asymmetry ($\rho_v = 4.9\%$). With increase in concentration the anisotropy decreases at first till we reach 0.6% concentration and increases again with further increase in the concentration reaching maximum asymmetry between 15 to 20% concentration. With further increase in concentration there is a very slow but detectable tendency for the aggregates to become less and less asymmetrical.

At very high concentrations, appreciable amounts of secondary and coherent scattering may be present in the observed scattered light. This makes the interpretation of the size and the shape of the individual scattering centres in terms of the intensity and depolarization more and more unreliable. It may be pointed out, however, that the gradual decrease in ρ_v at very high concentrations (above 15%) is in line with similar observations made by Katti (1951) during his investigations on concentrated solutions of gelatine, agar and cellulose acetate.

CONCLUSION

These investigations show that even in the pH range 8.0 to 7.0 the ions are in a state of aggregation, the actual size of the ions is possibly much less than $110\mu\mu$. In this range of pH Kestigian and Stein's absolute ionic weight results indicate ionic aggregates consisting, on an average, of 3 to 4 single molybdate ions. The initial constant ionic weight portion of Jander's ionic weight versus pH curve is supported by these investigations in the fact that no change in the size and shape of the ions is noticed in the pH region 8.0 to 7.0. With decrease in pH below 7.0 the size of the ionic aggregates increases, the maximum size of these aggregates occurring in the pH interval 4.0 to 2.5. The increase in the size of the aggregates is normally followed by a tendency of the aggregates to become more symmetrical.

An appreciable concentration effect on the anisotropy of the ionic aggregates is revealed by this investigation in the basic range, viz. 7.0 to 8.0 pH . It is very likely that the increased anisotropy in the pH range below 7.0 at high concentrations may be due to further aggregation of the smaller aggregates noticed in the solutions of the lowest concentrations. As the ρ_h values of the ions in the pH range 8.0 to 7.0 is about 100%, this growth cannot be followed by measurements on depolarizations only. In addition we have to make measurements on the scattering powers of these solutions as well before we can arrive at any definite conclusion regarding the changes in the size and shape of the aggregates in this pH range. This is being taken up.

Before concluding it is worth while pointing out that at very low concentrations the solvent contributes in a finite manner to the observed depolarizations and therefore should be taken into consideration, as is done by Kestigian and Stein.

As can easily be shown the corrections for the solvent scattering in the depolarizations can be made only if we make accurate determinations on the intensities and depolarizations of the solution and the solvent separately. Since in the present investigations we are dealing with concentrations mostly above 0.1%, the intensity measurements have not been made.

Similar investigations on Ammonium and Potassium molybdates are nearing completion and shall be reported in further papers.

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ABSTRACT

Extensive measurements on the depolarization of light transversely scattered by sodium molybdate solutions have been made by using the Krishnan light scattering technique in order to study the changes in the size and shape of the polymolybdate ions in basic and acidic solutions. The concentrations vary from 0.1% (very dilute solution) to 30% (highly concentrated solution nearing the solubility limit) and the *pH* values vary from 8.0 to nearly 0.5. Aggregation and dispersion of the polymolybdate ions in these solutions has been discussed in the light of the observations made.

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