

THE MEASUREMENT OF DIFFUSION RATES INSIDE FILTER PAPER AND ITS APPLICATION TO THE STUDY OF COMPLEXES IN SOLUTION

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INTRODUCTION

Diffusion measurements in porous media such as agar gel or stacks of filter paper disks have already been carried out by several workers¹ in order to determine the degree of polymerisation of organic substances. The rate of increase of the spot size on filter paper sheets was measured by others (for a review see ref. 2) in connection with problems of separability in electrophoresis or in work on quantitative determination by comparing spot sizes or spot lengths.

The work cited above indicated that the degree of polymerisation could be measured and that such measurements were sufficiently accurate. Hence it was considered desirable to utilise such measurements for the study of polyions in solution, since these techniques seem to be much faster and simpler than those usually employed in inorganic chemistry. In this paper first the technical problems of such diffusion measurements will be discussed. Then a report will be given of experiments to test these measurements by studying polyions which had already been studied by other methods and finally their application to the study of some new complex systems will be dealt with.

TECHNIQUE

A number of polyanions adsorb on cellulose paper³ but not on glass fibre paper and for this reason Whatman glass fibre paper was used throughout this investigation. The absence of adsorption was confirmed for each system studied by running an ascending chromatogram.

Squares of glass fibre paper (approx. 4 cm × 4 cm) are impregnated with the appropriate solution by dipping them into a petri dish containing the solution, after which the excess liquid is blotted off between filter papers. Three or four spots of 0.01 ml of the solution to be studied are spotted on the impregnated paper from an Agla micrometer syringe and the paper is then placed on a glass support and brought into a saturated atmosphere for a certain time. A number of desiccators holding the solution in which the diffusion is to be studied were used. After some preliminary work it became evident that the best results were obtained with spots which diffused for 0, 30 and 60 minutes.

The increase of the spot size shows a linear relationship with time. After one hour spots have a tendency to become too diffuse.

The paper squares are removed from the desiccator, sprayed with suitable colour reagents and then the spot area is measured by tracing the visible contours with pencil and copying them by means of carbon paper onto graph paper ruled in mm²; counting the squares provides the area in mm². In previous work⁴ with this method of measuring surface area on chromatograms an accuracy of $\pm 5\%$ was obtained. If, however, the spot areas are measured after only 0, 30 and 60 minutes, the contours are so sharp that in the hands of the author this method gives results with an average error of less than 3%.

DIFFUSION MEASUREMENTS WITH MOLYBDATE AND VANADATE SOLUTIONS

The first problems to be solved in this work were: to see whether the differences in spot area are sufficiently large to observe changes in polymerisation and whether the results obtained are identical with those obtained by other diffusion methods.

The variation of the spot size of molybdate and vanadate solutions with varying pH was selected, since these solutions had been studied previously by JANDER (for a summary see ref. 5).

(a) Molybdate

Acetate buffers prepared from *N* sodium acetate and *N* HCl were used as electrolytes; the molybdate solution consisted of the same buffer containing *M*/100 molybdate (molarity with respect to Mo) prepared from $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$.

TABLE I
DIFFUSION RATE MEASUREMENT OF A *M*/100 MOLYBDATE SOLUTION IN
SOLUTIONS OF DIFFERENT pH VALUES
The spot areas are in mm² and the values given are the averages of four spots.

pH	Spot area time = 0	Spot area time = 30 min	Spot area time = 60 min
7.8	24.3	108.6	185.6
6.9	23.2	113.3	184.0
6.6	21.7	103.9	158.0
6.0	24.0	87.3	141.3
5.2	21.0	91.2	155.3
4.9	22.0	83.3	143.3
4.19	21.2	62.0	99.0
3.49	21.0	63.0	97.3
3.09	20.0	57.6	97.0
2.32	20.0	57.0	97.3
1.85	19.2	58.3	96.6
1.42	19.3	58.0	95.2
1.24	19.0	45.3	71.0
0.91	18.3	37.6	61.0
0.75	17.0	33.3	56.0
0.65	18.0	36.3	62.6

Table I shows the spot areas (average values of 4 spots) measured at different pH values, after zero, thirty and sixty minutes, the paper having been sprayed with potassium ferrocyanide in HCl. JANDER⁵ used the equation $Dz\sqrt{M} = \text{constant}$

(D = the diffusion coefficient, z = the specific viscosity and M = the molecular weight) to calculate the molecular weights at various values of the pH. We have avoided such calculations for two reasons: firstly the mathematical treatment of spots with decreasing concentration is rather complicated and secondly the theoretical side of JANDER's work had been severely criticised. We thus contented ourselves with working out a method capable of detecting changes in molecular aggregation which need not necessarily correspond to polymer formation but may also be due to changes in ionisation, etc.

When the results shown in Table I are plotted in the same manner as those of JANDER using simply the spot areas as ordinates and the pH's as abscissae, they agree essentially with those obtained by JANDER. The spot size-pH and diffusion-pH curves are both shown in Fig. 1.

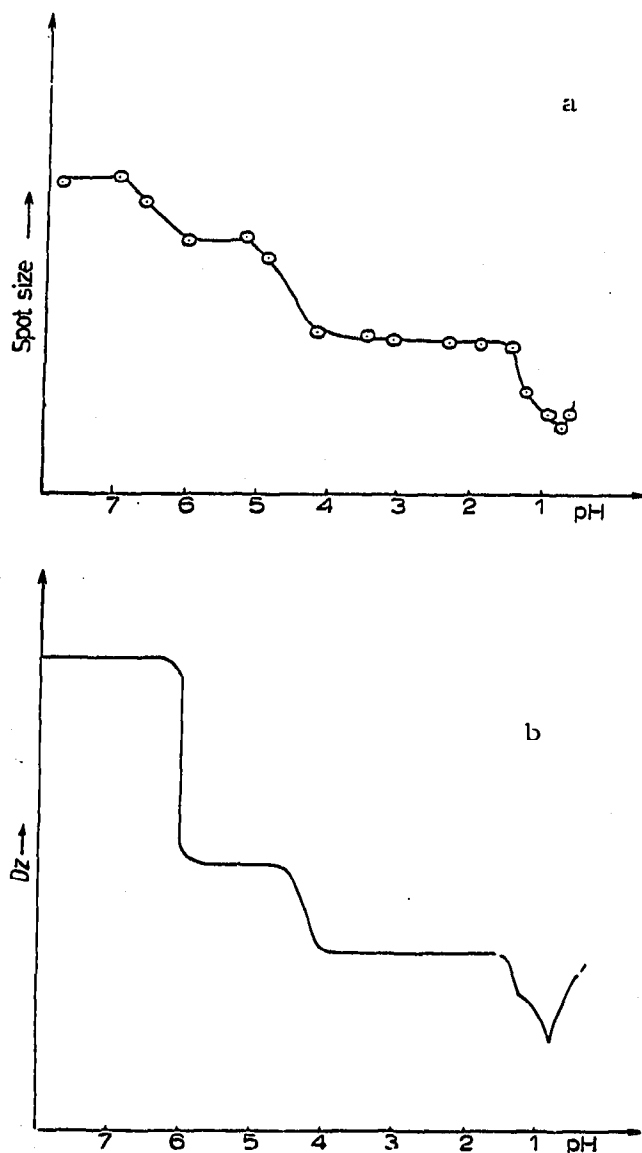


Fig. 1. (a) Spot size plotted against pH for molybdate in acetate-HCl buffers. (b) Diffusion plotted against pH from the experiments of JANDER⁵.

(b) Vanadate

Using the same technique and the same buffers, $M/100$ $\text{NaVO}_3 \cdot 4\text{H}_2\text{O}$ (molarity with respect to V) was studied. The best spots were obtained with a solution of KI in HCl as reagent. Fig. 2 shows the diffusion-pH curve obtained, and below it the diagram of ROSSOTTI AND ROSSOTTI⁶ for the vanadate system. The inflections coincide although in this system some changes are due to a change in the ionisation.

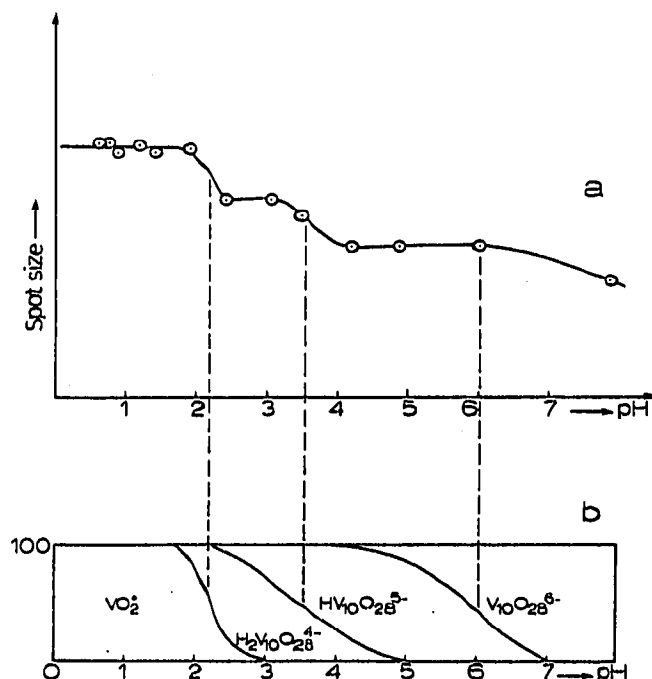


Fig. 2. (a) Spot size plotted against pH for vanadate in acetate-HCl buffers. (b) Diagram of ionic species distribution with variation of pH for vanadate according to ROSSOTTI AND ROSSOTTI⁶.

APPLICATION OF THE METHOD TO SOME COMPLEXING REACTIONS

For the two complexes discussed above we concluded that the spot area diffusion measurements are suitable to provide a simple although qualitative test for detecting changes in molecular aggregation. We have therefore employed it in a number of cases which happened to interest us, and these are listed below:

(i) Complexes of borate with mannitol

Fig. 3 shows the spot area variation of $0.05 M$ boric acid in aqueous solutions of mannitol (from $0.05 M$ to $0.5 M$ in $0.5 M$ NaCl). Two definite plateaux are formed, the first when the boric acid-mannitol ratio in the solution spotted is $1:1$ and the second after the ratio has become $1:2$. Therefore it seems that borate forms two complexes with 1 and 2 molecules of mannitol respectively.

(ii) Complexes of arsenic acid with mannitol

Arsenic acid ($0.038 M$ in $0.5 M$ NaCl) was allowed to diffuse into mannitol (up to $0.5 M$ in $0.5 M$ NaCl). Since arsenic acid is a relative strong acid we also measured the spot size of $0.038 M$ HCl placed on the same piece of glass fibre paper. There is a

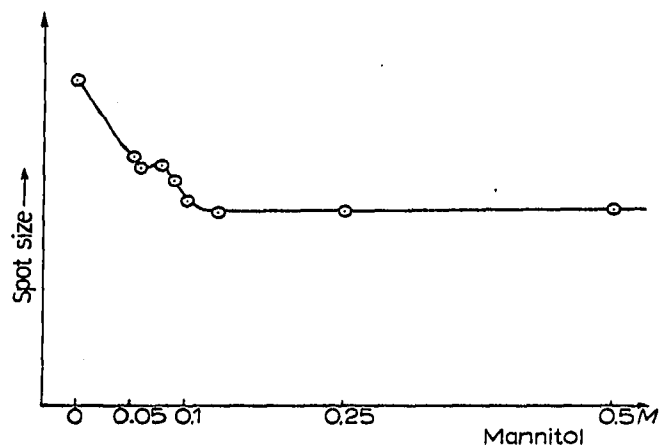


Fig. 3. Variation of spot size with the concentration of mannitol for solutions of boric acid in 0.5 M NaCl.

small change in the diffusion rate of HCl which, however, changes linearly with the concentration of mannitol. In Fig. 4 we have plotted the change of diffusion rate of spots of arsenic acid "corrected" for the diffusion rate of HCl. There is one single slope in the change of the diffusion rate and if the molecular weight of the final compound is calculated it is found to be (approx.) 331, the theoretical value for a 1:1 arsenic acid-mannitol complex being 324. Thus it seems reasonable to assume that in the region examined only a 1:1 complex is formed.

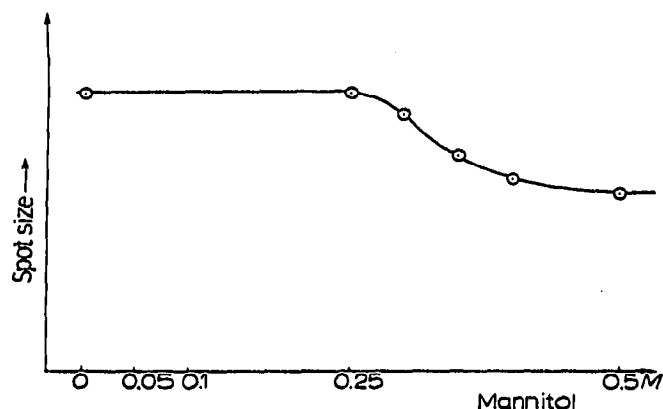


Fig. 4. Variation of spot size with the concentration of mannitol for solutions of arsenic acid in 0.5 M NaCl.

(iii) Complexes of platinum and palladium with stannous chloride

During paper electrophoretic⁷ and chromatographic⁸ work, it became obvious that the formula $(\text{PtSn}_4\text{Cl}_4)^{4+}$ suggested by AYRES *et al.*⁹ did not correspond to the species in solution. Diffusion experiments comparing H_2PtCl_6 in HCl and in $\text{SnCl}_2\text{-HCl}$ of identical ionic strength would suggest a molecular weight of approximately 900 for the platinum-stannous chloride complex. Since the complex is anionic we considered the following compounds as possible: $\text{H}_2\text{PtCl}_6 \cdot 2\text{SnCl}_2$ (mol. wt. 789), $\text{H}_2\text{PtCl}_6 \cdot 3\text{SnCl}_2$ (mol. wt. 978.7) and $\text{H}_2\text{PtCl}_6 \cdot 4\text{SnCl}_2$ (mol. wt. 1068.4). The diffusion rate would indicate that $\text{H}_2\text{PtCl}_6 \cdot 3\text{SnCl}_2$ is the most likely or perhaps the major species present.

(iv) HAuCl_4 and HgCl_2 in perchloric and sulphuric acid

Paper chromatographic studies suggested¹⁰ that HAuCl_4 and HgCl_2 may possibly form complexes with polyvalent acids such as H_2SO_4 . Diffusion experiments comparing the diffusion in HClO_4 and H_2SO_4 indicated that only negligible differences existed in the diffusion rates, thus complex formation of the type of heteropoly acids must be ruled out.

SUMMARY

A simple technique for measuring diffusion rates on glass fibre paper is described. This technique was shown to be suitable for the study of polyacid formation and complexing in solution.

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