on the neutral and basic side of the iso-electric point is therefore too short and indefinite to enable one to determine whether there is a similar maximum on this side of the iso-electric point, also.

Summary

The method of studying the cataphoresis of proteins by the U-tube method, determining the position of the protein layer by photographing its fluorescence when illuminated with ultraviolet light has been developed and used to measure the mobility of egg albumin at different acidities. Buffer mixtures of sodium acetate with acetic acid and of disodium hydrogen phosphate with citric acid were used over a range of P_H from 7 down to about 3 and 2.5, respectively.

The two buffer mixtures give similar results in general indicating a predominant influence of the hydrogen-ion concentration on the mobility. The sodium acetate and acetic acid mixture gives a broader region of minimum mobility, in which there is evidence of movement toward both electrodes.

The maximum mobility observed was toward the cathode 21.79×10^{-5} cm. per second at a P_H of 2.93.

Further studies by similar methods are in progress at the University of Wisconsin and at Upsala.

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[CONTRIBUTION FROM THE FAYERWEATHER CHEMICAL LABORATORY OF AMHERST COLLEGE]

MOHR'S METHOD FOR THE DETERMINATION OF SILVER AND HALOGENS IN OTHER THAN NEUTRAL SOLUTIONS

BY HOWARD WATERS DOUGHTY

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The well-known method of Mohr for the volumetric determination of silver and halides, using potassium chromate as indicator, has the serious limitation that it can be used only in neutral solution. The Volhard method, using ferric alum as indicator and ammonium thiocyanate to precipitate the silver, while applicable to acid solutions, has the disadvantage that when chloride is to be determined it is necessary to filter the silver chloride from an excess of silver nitrate and then titrate the excess of silver nitrate with thiocyanate. It is possible, of course, to use Mohr's method with a solution which is originally acid or alkaline by neutralizing exactly, using methyl red as indicator and titrating to the appearance of a yellow color, but the method is rather tedious.

Apparently it has not been realized that strict neutrality is not necessary for the successful use of Mohr's method. This method depends upon the difference in solubility of silver chromate and silver halide (chloride, bromide or iodide). Silver chromate is insoluble in water, but dissolves readily in acids, even acetic acid. The solubility, however, is not a function of the amount of acid present, but depends upon the hydrogen-ion concentration. In solutions having a Sörensen value (P_H) of 5 to 7, silver chromate is not appreciably soluble and it occurred to the writer that if this P_H value is established by use of a suitable buffer, no difficulty should be found in dealing with other than neutral solutions by the Mohr method. The results have been entirely satisfactory and by use of a sodium acetate (2 mols.)—acetic acid (1 mol.) buffer, giving P_H about 5.5, silver nitrate can be titrated against hydrochloric acid as easily and as accurately as against sodium chloride. A larger proportion of sodium acetate may be used, giving P_H nearer to 7, but excellent results are obtained with the 2:1 buffer.

Procedure.—If the unknown solution is acid to congo red or methyl orange (test paper), add normal sodium acetate solution until it is alkaline to these indicators, though still acid to litmus. Then add 20 cc. of the buffer solution, prepared by dissolving 2 moles (136 g.) of crystallized sodium acetate and 1 mole (60 g.) of glacial acetic acid in water and diluting to one liter. If the unknown solution is alkaline to litmus or phenolphthalein, add acetic acid until the solution is acid to these indicators though still alkaline to congo red or methyl orange, using test paper. Then add 20 cc. of the buffer solution as before. In standardizing silver nitrate against hydrochloric acid or *vice versa*, it is only necessary to put 20 cc. of the buffer into the flask or casserole before starting the titration if the solutions are approximately 0.1 *N*, but if stronger solutions are used it is well to add a corresponding amount of sodium acetate.

In any case, after addition of the buffer solution, add two or three drops of potassium chromate solution (free from chloride) and proceed with the titration as usual in using Mohr's method, but using 0.1 *N* hydrochloric acid instead of sodium chloride, if more convenient.

Owing to the large concentration of ionized salts due to the addition of the buffer, the silver halide is likely to coagulate and thus obscure the end-point, leading to the use of a slight excess of silver nitrate. This coagulation may be prevented easily by the well-known method of adding three or four drops of capryl alcohol before starting the titration.

Experimental.[1]—A solution of hydrochloric acid was standardized by the iodate-iodide method of Bertiaux[2] and found to be 0.1077 *N*. The same value was found by comparison with 0.1 *N* sodium hydroxide solution, which had been standardized by a hydrochloric acid solution

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[1] The writer wishes to express his thanks to Mr. J. R. Bates for his assistance in testing this method in the laboratory.

[2] Bertiaux, *Bull. soc. chim.*, **27**, 697 (1920); *C. A.*, **14**, 3615 (1920).

which in turn had been standardized gravimetrically. A silver nitrate solution was standardized by Mohr's method against weighed pure sodium chloride and found to be 0.0925 *N*. This silver nitrate was then titrated against the 0.1077 *N* hydrochloric acid by the procedure just described, using 20 cc. of the buffer solution, and found to be 0.0925 *N* thus agreeing exactly with the previous standardization against pure sodium chloride by the ordinary Mohr's method. In all titrations, duplications were quite as close and end-points as clear as in the ordinary use of the Mohr method in neutral solution.

The presence of copper interferes with the end-point of this reaction, owing to the fact that the solubility of copper chromate is of the same order of magnitude as that of silver chromate and this is true generally of the heavy metals and barium. The method also fails in the presence of easily oxidized substances that react with the chromate ion.

Summary

A modification of the Mohr method for volumetric determination of silver and the halogens is described. By the use of a sodium acetate-acetic acid buffer the P_H value of the solution is kept between 5 and 7, thus extending the use of the Mohr method to solutions other than neutral.

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[CONTRIBUTION FROM THE LABORATORY OF COLLOID CHEMISTRY, UNIVERSITY OF WISCONSIN]

A NEW METHOD FOR THE DETERMINATION OF THE DISTRIBUTION OF SIZE OF PARTICLES IN EMULSIONS[1]

BY ELMER O. KRAEMER AND ALFRED J. STAMM

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It has been pointed out by Svedberg[2] that the adequate characterization of a colloid solution requires a knowledge of the distribution of size of particles in the colloid system. Since the particles of a colloid system are usually not susceptible to direct microscopic measurement on account of their small size, the determination of the distribution of size of particles generally depends upon the application of the resistance-to-motion law, $f = 6\pi\eta rv$, where f is the friction developed when a sphere of radius r moves with the uniform velocity v in a liquid possessing the viscosity η.[3]

Very few such studies have been made upon emulsions in which the disperse phase rises under the influence of gravity. The methods which

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[1] An abstract of this paper was presented before the Second National Colloid Symposium, Northwestern University, June, 1924.

[2] Svedberg and Estrup, *Kolloid-Z.*, **9**, 259 (1911).

[3] Svedberg gives an excellent discussion of the determination of distribution of size of particles in his book (a) "Colloid Chemistry," American Chemical Society Monograph, Chemical Catalog Co., **1924**.