THE ELECTRICAL CONDUCTANCE AND THE KINETICS OF PRECIPITATION IN THE REACTION OF BARIUM HYDROXIDE WITH OXALIC ACID

WALTER W. LUCASSE, JOHN G. MILLER, AND EDGAR L. ECKFELDT¹

Department of Chemistry and Chemical Engineering, University of Pennylsvania, Philadelphia, Pennsylvania

Received February 7, 1949

Studies of the electrical conductance of various types of systems have been made in numerous cases in order to obtain fundamental data, such as the solubility of slightly soluble substances and the dissociation constants of weak acids and bases, or to shed light upon the physicochemical nature of the materials involved, such as the basicity of polyvalent acids and the strength of electrolytes. The feasibility of conductometric measurements for obtaining the end points of titrations in water solutions has been fully established and extension of the method to non-aqueous media has been indicated (9). In addition to this basic application, insight into the course of the chemical process can frequently be obtained from the change in the conductance of the system in which the titration is taking place (1).

The present paper is concerned with the reaction of barium hydroxide and oxalic acid. It has already been shown that the end point of the conductometric titration of oxalic acid with barium hydroxide is quantitative (6), and conductance curves for the titration of the salts of several metals with lithium oxalate and ammonium oxalate are well known (3, 8). However, no detailed conductance measurements of the acid-base titration have been published hitherto, nor has the nature of the process been adequately considered.

Ideally, the titration should be a simple one showing, for the complete neutralization of the oxalic acid, a single sharp end point according to the scheme:

$$H_2C_2O_4 + Ba(OH)_2 \rightarrow BaC_2O_4 + 2H_2O$$

Indeed, the measurement would appear to be useful not only for exact but for rapid estimation of the oxalic acid content in aqueous solution because of the marked change in the nature and number of the ions accompanying the process. During the neutralization, a large decrease in conductance might be expected through loss of both of the ions of the rather strong electrolyte, oxalic acid, particularly since one is the highly conducting hydrogen ion. Beyond the end point, addition of an excess of free barium and hydroxyl ions would cause a correspondingly large increase in conductance. Furthermore, such a picture would not indicate the modifying formation of the acid oxalate of the dibasic acid $(K_1 = 5.02 \times 10^{-2}; K_2 = 5.18 \times 10^{-5} \text{ at } 25^{\circ}\text{C.})$. In case it were formed, its relatively high solubility, together with its instability in the absence of an excess of the acid (5), would seem to preclude any difficulty due to the precipitation of that substance.

¹ Present address: Leeds & Northrup Company, Philadelphia, Pennsylvania.

Actually, as described by the work reported here, the conductance titration of this system, although giving a quantitative end point under proper conditions, is not convenient for routine analytical work. As anticipated, the formation of the acid oxalate introduces no complicating factors. However, soon after the process reaches the half-neutralization point, the conductance readings change slowly with the time. These changes and the behavior of the precipitate, during the part of the process in which decreasing conductance takes place, prompted the study here reported.

PROČEDURE

In order to obtain an explanation of the variation of the conductance with the time, the reaction was not followed by the usual titration method. According to such procedure, a series of additions of standard barium hydroxide solution would have been added to a single starting solution of oxalic acid until well beyond the point of complete neutralization. Instead, separate solutions of both reactants were used for each datum point on the curve representing the entire titration. This procedure avoids the difficulty that would be met in following the usual method of conductometric titration whereby the condition of the system, especially the presence of a precipitate prior to the addition of the second constituent, would influence the effect of the added substance. Furthermore, a kinetic study of the process requires the procedure followed in order that the concentration of the reactants be known as a function of the time and that the system be studied near the zero of reaction time. Finally, the use of separate solutions provides an excellent check on the individual points making up the entire curve.

The reaction was studied at two temperatures, 25°C. and 50°C. The apparatus used was of a simple type (11) and the chemicals were of high quality and not further purified. The conductance values on which the plots are based are the measured values of the actual cell resistances in reciprocal ohms. The constant for the cell used throughout the study, 0.198, was introduced in the calculation of the specific conductance of the saturated barium oxalate solution.

Exactly 10 cc. of the same stock solution of approximately 0.4 N oxalic acid was added to exactly 200 cc. of water for each measurement. Identical concentration of these starting solutions was evidenced throughout by the virtual equality of their conductance. The exact desired amount of barium hydroxide was next added rapidly from a buret. This solution was taken from the supernatant liquid in equilibrium with the solid phase and was slightly over 0.4 N, the solubility of barium hydroxide at room temperature being 0.44 N. The solutions were stirred uniformly during the whole procedure. The conductance was determined at once to obtain an initial value for the reacting system. As will be seen later, the change in conductance with time when this occurred was ordinarily of such a character as to allow an observation of the conductance very close to the initial value. In those instances where the changes at the beginning were more rapid, the initial value was estimated by extrapolation.

Almost continuous reading of the conductance was then made and values were recorded to the nearest second at intervals suited to the rate of change. A typical velocity curve is shown in figure 1, which pictures the change in conductance taking place at 25°C. upon the single addition of 6.60 cc. of base to the acid solution. In all cases the conductance approached a well-defined value, as shown in the figure, in a period no longer than 15 min.

No decrease in conductance occurred on the addition of less than 3 cc. of base and no conductance change took place unless accompanied by precipitation. Up to equivalence any initial precipitate, probably due to locally high initial concentrations of barium hydroxide, dissolved immediately. Thus such solutions started effectively clear, slowly became cloudy, and finally became turbid. Past the point of equivalence the systems contained precipitate from the start.



FIG. 1. The change of conductance with time (addition of 6.60 cc. of base to 10 cc. of acid at 25°C.).

The experimental results of the study of the entire concentration range are summarized in figure 2. Only the initial and final conductance values are shown for each system. The two plots, the upper showing the data at 50°C. and the lower those at 25°C., are quite similar in form. In each case, since there was no change in conductance with time up to the half-neutralization point, a single curve shows the conductance of the system as a function of the amount of barium hydroxide added. Beyond this point, the curve branches and shows markedly different initial and final conductances at each concentration. Between the halfneutralization point and the end point, the curves for the initial conductances show relatively little change in contrast with the continuing sharp decrease in the curves for the final conductances. Beyond the end point, the curves for the initial and final conductances are almost parallel. Speculations as to the physicochemical nature of the system can be drawn from consideration of the curves over the entire range, from comparison of the slopes of the curves for the initial and final



conductances and, finally, from study of the slopes of the curves at the two temperatures over the three concentration ranges of added base.

The curves of the final conductance values have a sharp inflection occurring

at the same end point at both temperatures. At 25°C. the specific conductance at this point $(1.2 \times 10^{-4} \text{ mho cm.}^{-1})$ is in satisfactory agreement with the value quoted (1) by Britton, 1.086×10^{-4} , corrected for the solvent, and those obtained by Kohlrausch (7) for saturated solutions of barium oxalate at 23.3° and 28.4°C., namely, 1.011×10^{-4} and 1.264×10^{-4} , respectively, and the value at 50°C. shows the effect of increased solubility (4). The greater slopes of the curves at the higher temperature reflect the increase in the mobility of the ions with rise in temperature.

PHASE CHANGES DURING THE PRECIPITATION

In seeking an explanation of the conductance and phase changes during the precipitation process, it would appear that these are due primarily to a physical rather than a chemical change. Possible chemical changes considered for this range of the process (B in figure 2) were, first, the initial formation of barium acid oxalate followed by its decomposition into the normal oxalate, thus

$$2H_2C_2O_4 + Ba(OH)_2 \rightarrow Ba(HC_2O_4)_2 + 2H_2O$$
$$Ba(HC_2O_4)_2 \rightarrow \underline{BaC_2O_4} + H_2C_2O_4$$

and second, the formation of auto-complexes, as follows:

$$2BaC_2O_4 \rightarrow Ba[Ba(C_2O_4)_2]$$

The first of these may be eliminated by the fact that both reactions of this se quence are rapid (2) and also because the experimental procedure used was such that the direct formation of the normal oxalate would ordinarily be expected. The second possibility may be dismissed in view of the small tendency reported (12, 13) for barium oxalate to form complexes with itself, despite the existence of oxalato complexes with other metals. Furthermore, the rate of conductance change did not appear to be sensitive to temperature change, a fact which tends to oppose the idea of a chemical reaction as basis for the change in conductance.

Evidence shown below indicates that a physical change causes the variation of the conductance with time: namely, the change of normal barium oxalate from the dissolved state in the form of conducting ions in a supersaturated solution to the solid state as a precipitate. From this viewpoint, the general form of the curves and the relation of the initial and final conductances is clarified. Up to the half-neutralization point (the range A in figure 2), the reaction taking place, in all probability, is to be written as follows:

$$2\mathrm{H}_{2}\mathrm{C}_{2}\mathrm{O}_{4} + \mathrm{Ba}(\mathrm{OH})_{2} \rightarrow \mathrm{Ba}(\mathrm{HC}_{2}\mathrm{O}_{4})_{2} + 2\mathrm{H}_{2}\mathrm{O}$$

This explains the regular decrease in conductance with increase in amount of added barium hydroxide and also the fact that at each point the initial and final conductances are the same.

Past this point, that is, over the range B, the reaction forms the normal oxalate to an extent dependent on the degree to which the half-neutralization point has been exceeded:

$$H_2C_2O_4 + Ba(OH)_2 \rightarrow BaC_2O_4 + 2H_2O$$

1402

Over the initial part of the range, a comparatively small amount of the oxalate group is available for reaction with the barium; the balance is associated with the second hydrogen of the dibasic acid. As the end point is approached, the relative proportions are reversed.

If the oxalate formed did not precipitate, but remained in solution, the process should change the conductance of the system but little from that at the halfneutralization point. The net effect, in the absence of precipitation, would be merely the replacement of the HC_2O_4^- ion by the C_2O_4^- ion and the addition of an extra Ba⁺⁺ ion. Indeed, this is in accord with the slight rise in the initial conductance over this range, as seen especially in the 50°C. curve. Of course, precipitation eventually takes place and removes both barium and oxalate ions, leaving only the ions of barium acid oxalate and of its decomposition product, oxalic acid, which explains the slight decrease in slope of the final conductance curve after the half-neutralization point is passed.

After equivalence (over the range C), the addition of excess barium hydroxide produces an initial conductance curve increasing almost parallel to the final conductance curve. This is also in accord with the precipitation mechanism, since here from the very start an excess of hydroxyl ions is present and to a greater degree the farther the system is past the equivalent point. Thus, initially, in comparison with the region preceding equivalence, the barium and oxalate ions are present with an excess of both barium and hydroxyl ions, and the amount of barium oxalate to be precipitated is constant in this region. With a constant amount to be precipitated, a constant decrement between the initial and final conductances might be predicted, that is, the curves should be expected to be parallel.

KINETICS OF THE PRECIPITATION

Turning now to a consideration of the precipitation process which causes the slow decrease in the conductance by the combination of the barium and oxalate ions and their removal into a solid phase, some qualitative evidence may first be given. In addition to the fact that the velocity of change of conductance is little affected by temperature, it was noticed that the rate is increased by stirring, a behavior typifying a precipitation process. Because of this effect, the stirring was maintained as constant as possible throughout the measurements.

Additional evidence comes from titrations involving oxalates (8), in which it is reported that the presence of alcohol speeds up the titration because it lowers the solubility of the oxalate formed and prevents the formation of supersaturated solutions. Conversely, it would be expected that substances such as gelatin and tannic acid, which inhibit precipitation, would slow the process of change in conductance. These were tried but, unfortunately, chemical interaction took place with the components of the system and made the results indefinite. However, focusing on the present work, it would appear from the studies mentioned that oxalates have a tendency to form supersaturated aqueous solutions.

From a quantitative standpoint, a theoretical treatment of the process gives a satisfactory explanation of the rate of change of the conductance of the system and thus, presumably, of its concentration. In this treatment it is assumed throughout that the change in conductance of the system is proportional to the change in concentration of normal barium oxalate in solution as precipitation from the supersaturated solution takes place. The precipitation is pictured to be dependent in rate upon both the concentration of the dissolved oxalate and the total surface area of the precipitate present. These factors are well known to affect the rate of precipitation from supersaturated solutions such as are postulated in this case.

Figure 1 shows that the precipitation begins very slowly, gains speed, attaining the maximal value in the mid-region, and then slows down again as the process approaches completion. The slow rate at the beginning may be attributed to the very small initial surface area of the solid phase. As precipitation progresses the amount of solid, and consequently its area, increases so that the process is greatly accelerated. However, as the supersaturated solution becomes depleted of the barium oxalate, diminishing the driving force of the excess concentration, the speed again decreases.



FIG. 3. General type of sigmoid curve and concentration range

The sigmoid curve of figure 3 symbolizes the type of change which is being considered. The concentration of the solution changes between the limits indicated by the two horizontal dotted lines, I and F, I being the initial and F the final concentration. At any intermediate point the concentration has the value c at the corresponding time, t. The rate of change of c at this point depends upon the surface area of the precipitate and upon the effective concentration still available to drive the process forward. Since the area increases as the square of a particular dimension while the volume increases as the cube of the same dimension, the change in the area of the precipitate will be proportional to the change in the area of precipitate raised to the two-thirds power. The amount of precipitate is proportional to the difference I - c; hence the changing area function will be proportional to this difference raised to the two-thirds power.² The effective

² In a study of the kinetics of precipitation of vanadic acid from supersaturated solutions, N. N. Petin (Sci. Repts. Moscow State Univ. **1936**, No. 6, 43-7), assuming the process of crystallization to be made up of nuclei formation and crystal growth, proposed that the rate of the latter process is proportional to the surface area of the growing crystals and hence to the amount of the precipitate. Upon testing equations in which it was assumed

concentration still available to drive the process forward is proportional simply to the difference c - F. Expressing these concepts as an equation leads to

$$-\frac{dc}{dt} = k(I-c)^{2/3}(c-F)$$
(1)

in which k is a constant, which might be termed the velocity constant.

$y \qquad \int_{0.6}^{y} \frac{-dy}{y(1-y)^{2/3}} \qquad y \qquad \int_{0.6}^{y} \frac{-dy}{y(1-y)^{2/3}}$	
0.99 -1.856 0.45 0.472	
0.98 -1.687 0.40 0.643	
0.97 -1.566 0.35 0.825	
0.96 -1.469 0.30 1.026	
0.95 - 1.386 0.25 1.252	
0.94 -1.313 0.20 1.516	
0.92 -1.185 0.16 1.771	
0.90 -1.076 0.13 2.00	
0.87 - 0.931 0.10 2.29	
0.84 - 0.804 0.08 2.52	
0.800.650 0.07 2.67	
0.75 - 0.475 0.06 2.83	
0.70 - 0.311 0.05 3.02	
0.65 - 0.154 0.04 3.25	
0.60 0 0.03 3.55	
0.55 0.154 0.02 3.96	
0.50 0.310	

 TABLE 1

 Values of the integral obtained by graphical integration

Rearranging and integrating equation 1 gives

$$t = \frac{1}{k} \int \frac{-\mathrm{d}c}{(I-c)^{2/3}(c-F)}$$
(2)

An elliptical integral of this form cannot be expressed in terms of elementary functions, and before obtaining values of the definite integral it is expedient to simplify the equation by defining a new variable:

$$y = \frac{c - F}{I - F} \tag{3}$$

The quantity y is obviously the ratio of the concentration change still to take place at the time t to the total concentration change; or in terms of the process, it is the fraction which, at the time t, still remains to be completed. Upon substitution in equation 2, it follows that

1405

that the effect was proportional to the amount raised to the two-thirds, the first, and the one-third power, the most satisfactory agreement was found in the second case. His investigation, however, was concerned with relatively few points and the equations were applied in the mid-region rather than over the entire range.

W. W. LUCASSE, J. G. MILLER AND E. L. ECKFELDT

$$t = \frac{1}{k(I-F)^{2/3}} \int \frac{-\mathrm{d}y}{y(1-y)^{2/3}} = k_1 \int \frac{-\mathrm{d}y}{y(1-y)^{2/3}}$$
(4)

It can be shown that the integral of equation 4 passes through an inflection point when y equals 0.6 and this point, therefore, was chosen as one of the limits in the integration of the equation. Table 1 gives values of the integral of equation 4 obtained graphically. By means of these values, an equation for a particular case can be written and tested. The theoretical rate of a given precipitation is represented by the equation

$$t = k_1 \int_{0.6}^{y} \frac{-\mathrm{d}y}{y(1-y)^{2/3}} + k_2$$
 (5)

in which k_2 is the constant of integration.

The values of the constants of equation 5 are required before the equation can be applied to a specific case, but they can be evaluated readily from a plot of the data such as that in figure 1. The constant k_1 may be obtained by writing

$$k_{\rm I} = \frac{y(1-y)^{2/3}}{\left(-\frac{\mathrm{d}y}{\mathrm{d}t}\right)} \tag{6}$$

The numerator of the right-hand member of this equation is equal to 0.326 when y is 0.6 and, since this represents the inflection point, the corresponding value of the denominator is the steepest slope of the plot of the data. It is convenient and satisfactorily accurate to measure the slope graphically. k_1 having been obtained in this manner, k_2 may also be obtained from the plot. The value of this constant is equal to the time when the curve passes through the point where y equals 0.6.

The experimental results of figure 1 were used to establish the particular constants and this precipitation, accordingly, is expressed by the following theoretical equation:

$$t = 45 \int_{0.6}^{y} \frac{-\mathrm{d}y}{y(1-y)^{2/3}} + 117$$
 (7)

in which the time, t, is expressed in seconds. The smooth curve of figure 4 is a plot of equation 7. The experimental points have been superimposed on this plot to show the satisfactory agreement between the observations and the requirements of the theory described for the precipitation.

Further substantiation of this theory was given by experiments in which the surface area was kept large and constant by having present initially an amount of precipitate about two and one-half times the amount formed during the process studied. In such cases, the rate should be first order with respect to the concentration. That this is nearly true is shown by plots of the logarithm of the conductance change against the time. Such curves as represented in figure 5 were obtained, showing the required linearity, especially over the initial region of change.

These experiments, carried out in the presence of excess of precipitate, were rather difficult to control owing to the rapidity of precipitation. For this reason,

1406





FIG. 5. The rate of precipitation of barium oxalate

it was deemed advisable to study the precipitation of a similar barium salt where the solubility would be greater. After preliminary trials with several others, barium succinate was chosen.

The greater solubility of this salt required modification of the procedure. Barium hydroxide was run into 100 cc. of approximately 0.4 N succinic acid until neutralization occurred. The precipitate was allowed to form completely and an additional 10 cc. of succinic acid was added. The system was stirred until constant conductance resulted. Now 10 cc. of barium hydroxide was added and the conductance taken with time. Stirring was constant throughout.



FIG. 6. The rate of precipitation of barium succinate

The data obtained are plotted in figure 6, from which it will be seen that the curve is substantially linear over a large part of the change. The concavity upward, similar to that encountered with barium oxalate, may be due to the approach to the saturation point. This concentration is rather considerable and in such cases the process would correspond to an equilibrium process rather than to one going virtually to completion. Other factors (10) leading to non-linearity, such as adsorption of solutes on the precipitate, conductance due to suspended solid particles, and change in the solubility of the solid formed with change in the particle size of the precipitate should have relatively minor effects.

SUMMARY

The chemical and physical aspects of the reaction of barium hydroxide with oxalic acid have been investigated. The method of study was conductometric, and it has been shown that in the region where the conductance decreases with the time, the changes are primarily due to precipitation of normal barium oxalate from the supersaturated solution. Theoretical treatment of the kinetics of the precipitation has indicated that the rate is proportional to the concentration of the dissolved barium oxalate and to the surface area of the precipitate present.

REFERENCES

- (1) BRITTON, H. T. S.: Conductometric Analysis. D. Van Nostrand Company, Inc., New York (1934).
- (2) BRUHNS, G.: Z. anorg. allgem. Chem. 95, 194 (1916).
- (3) FREAK, G. A.: J. Chem. Soc. 115, 55 (1919).
- (4) Gmelin's Handbuch der anorganischen Chemie, 8 Aufl., S.-N. 30: Ba. Verlag Chemie, Berlin (1932).
- (5) GROSCHUFF, E.: Ber. 34, 3313 (1901).
- (6) HARNED, H. S., AND LAIRD, C. N.: J. Am. Chem. Soc. 40, 1213 (1918).
- (7) KOHLRAUSCH, F.: Z. physik. Chem. 64, 162 (1908).
- (8) KOLTHOFF, I. M.: Z. anal. Chem. 62, 161 (1923).
- (9) LUCASSE, W. W., AND ABRAHAMS, H. J.: J. Chem. Education 7, 341 (1930).
- (10) MAY, D. R., AND KOLTHOFF, I. M.: J. Phys. Colloid Chem. 52, 836 (1948).
- (11) MILLER, J. G., AND LUCASSE, W. W.: J. Chem. Education 22, 565 (1945).
- (12) MONEY, R. W., AND DAVIES, C. W.: J. Chem. Soc. 1934, 400.
- (13) Scholder, R., Gadenne, E., and Niemann, H.: Ber. 60, 1510, 1525 (1927).

THE ADSORPTION OF FATTY ACIDS ON CARBON BLACKS. CALCULATION OF PARTICLE SIZE¹

HILTON A. SMITH AND R. B. HURLEY

Department of Chemistry, University of Tennessee, Knoxville, Tennessee

Received February 7, 1949

INTRODUCTION

A great many studies have been made which deal with the adsorption of fatty acids on various types of activated charcoal. In general, the adsorption follows the Freundlich equation quite well. The actual adsorption characteristics depend on the particular fatty acid used and the solvent from which adsorption takes place (3). The adsorption is certainly affected by the porous nature of the adsorbent, and much of the surface is inaccessible to the fatty acid molecules.

Carbon blacks, on the other hand, are considered to be compact, non-porous particles, and the entire surface of these should be accessible to the adsorbate.

¹ Contribution No. 65 from the Department of Chemistry, University of Tennessee.