[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE CITY COLLEGE OF NEW YORK]

The Coprecipitation of Barium Ion with Hydrous Aluminum, Chromic and Ferric Oxides in the Presence of Ammonium Ion

BY LEO LEHRMAN, JEROME BEEN AND MILTON MANES

It is well-known that in systematic qualitative analysis considerable amounts of barium are lost before its detection.[1] This loss vitally affects a quantitative analysis of this cation and must be taken into account in such a determination. The cause has been attributed by some to the following two factors, which result in the precipitation of barium compounds: (1) oxidation of sulfide ion to sulfate ion in both the hydrogen sulfide and ammonium sulfide groups; (2) absorption of carbon dioxide by the alkaline ammonium sulfide solution.[2] However, some preliminary experiments showed that in the ammonium sulfide group in the presence of ammonium salts, which is usually the case, neither of the above effects was involved. Yet the amount of barium recovered in the filtrate was less than in the original solution. In the ammonium sulfide group there are two kinds of precipitates, hydrous oxides and sulfides. Inasmuch as they might act differently, it was decided to study them separately.[3]

When a precipitate forms, several causes, *i. e.*, occlusion, mixed crystal formation, solid solution, surface adsorption, compound formation and postprecipitation, might account for the retention (coprecipitation) of soluble material.[4] One or more of these causes might account for the coprecipitation of barium ion by the hydrous oxides. Since they are either amorphous or consist of extremely minute crystals, it is quite likely that surface adsorption takes place. This is especially probable in an alkaline solution where the precipitates would be negatively charged and therefore favor the adsorption of cations.[5] Furthermore, it has been shown that ammonium ion has an effect on the coprecipitation of other cations with hydrous oxides.[6]

The purpose of our investigation was to determine what factors cause the loss of barium ion so that they might eventually be removed.

Experimental

For the metal ions, solutions of chlorides made from reagent grade material were used. All solutions were tested for sulfate ion and found to contain a negligible amount. All experiments were run in duplicate. If the results did not agree, the experiments were repeated.

Precipitation of Barium Due to Absorption of Carbon Dioxide by an Ammonia Solution in the Presence of Ammonium Chloride.—To 5 ml. of barium chloride solution, equivalent to 40 mg. of barium, was added 1 g. of ammonium chloride, 10 ml. of concentrated ammonia solution, the volume made up to 25 ml. with water and allowed to stand in an open flask. A similar solution was prepared and put in a stoppered flask. These two experiments were duplicated, only the amount of ammonium chloride was 4 g. After three hours all the solutions were perfectly clear. In the open flasks after one day, a small amount of precipitate was present in the solution containing 1 g. of ammonium chloride, while the other had a slight but visible one. The precipitation increased very slowly the longer (in days) the flasks remained open. In the stoppered flasks no precipitation occurred even after fourteen days. It is seen that a rather long period of time is necessary before enough carbon dioxide is absorbed to cause precipitation of barium carbonate in the presence of ammonium salts. This is much longer than the usual time for filtering and washing.

The Retention of Barium by Precipitated Hydrous Aluminum, Chromic and Ferric Oxides.—To 50 mg. of aluminum ion and 100 mg. of chromic and ferric ions, separately, were added 1 g. of ammonium chloride, varying amounts of barium ion from 8–40 mg. and 5 ml. of 0.02% gelatin solution.[7] The solutions were heated to boiling, 5 ml. of concentrated ammonia added, which is an adequate excess to ensure complete precipitation, and the final volumes made up to 25 ml. The solutions were filtered and the precipitates washed with distilled water until free of barium ion. The number of washings varied from 8 to 12 of 15 ml. each. Though the hydrous ferric

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(1) Curtman and Frankel, THIS JOURNAL, **33**, 724 (1911).

(2) (a) Curtman and Frankel, *ibid.*, **33**, 724 (1911); (b) Zolotukhin, *Acta Univ. Vorogiensis*, **9**, 69 (1937).

(3) The experiments with sulfides will be described in a later paper dealing with the behavior of these substances.

(4) (a) Fajans and Beer, *Ber.*, **46**, 3486 (1913); (b) Paneth, *Physik. Z.*, **15**, 924 (1914); (c) Kolthoff, *J. Phys. Chem.*, **36**, 860 (1932); (d) Kolthoff, *Chem. Rev.*, **17**, 293 (1935); (e) Kolthoff, *J. Phys. Chem.*, **40**, 1027 (1936); (f) Schneider and Rieman, THIS JOURNAL, **59**, 354 (1937); (g) Karaoglanov, *Ann. univ. Sofia II, Livre* **2**, **34**, 81 (1937–1938).

(5) (a) Dhar, Sen and Chatterji, *Kolloid Z.*, **33**, 29 (1923); (b) Weiser, "The Hydrous Oxides," McGraw-Hill Book Co., New York, N. Y., 1st ed., 1926, p. 403–406; (c) Charriou, *J. chim. phys.*, **23**, 621, 673 (1926).

(6) (a) Weiser, "The Hydrous Oxides," McGraw-Hill Book Co., New York, N. Y., 1st ed., 1926, p. 406; (b) Charriou, *J. chim. phys.*, **23**, 621, 673 (1926); (c) Kolthoff and Stenger, *J. Phys. Chem.*, **36**, 2113 (1926); (d) Kolthoff and Moskovitz, *ibid.*, **41**, 629 (1937). This article contains a condensed review of the literature on this effect. (e) Kolthoff and Overholser, *ibid.*, **43**, 767, 909 (1939).

(7) The gelatin made it possible to wash the precipitates with distilled water with very little peptizing action; Caldwell and Moyer, THIS JOURNAL, **57**, 2372 (1935).

oxide required the most and the hydrous aluminum oxide the least, the former filtered and was washed much quicker. The filtrate and washings were evaporated to about 10 ml., filtered to remove small amounts of the precipitates that might have passed through and the filter paper washed until free of barium ion. The filtrate and washings were concentrated to about 10 ml., the barium precipitated as barium sulfate in special, calibrated tubes[8] and allowed to settle overnight. The amount of barium was determined first by measuring the height of the precipitate. This was compared with an equal height of barium sulfate in a similar tube, representing a known amount of barium, precipitated under the same conditions. Before using this rapid method, its accuracy was tested gravimetrically and found to give comparable results. It was noted that the height of the precipitated barium sulfate is a linear function of the amount of barium. Table I shows the results obtained.

TABLE I

THE RETENTION OF BARIUM ION BY HYDROUS ALUMINUM, CHROMIC AND FERRIC OXIDES

Metal	Ba^{++} used, mg.	Ba^{++} in filtrate, mg.	Ba^{++} lost, mg.
Al^{+++}	40	32	8
Al^{+++}	32	24	8
Al^{+++}	24	16	8
Al^{+++}	16	9.5	6.5
Al^{+++}	8	4	4
Cr^{+++}	40	30	10
Cr^{+++}	32	22	10
Cr^{+++}	24	14	10
Cr^{+++}	16	8	8
Cr^{+++}	8	3.5	4.5
Fe^{+++}	40	15	25
Fe^{+++}	32	9	23
Fe^{+++}	24	5	19
Fe^{+++}	16	3	13
Fe^{+++}	8	1.5	6.5

Figure 1 is the graph obtained by plotting the amount of barium found in the filtrate as abscissa and the amount retained (lost) by the different hydrous oxides as ordinates. It is a typical Freundlich isotherm, probably showing adsorption, inasmuch as the precipitations take place under fairly constant conditions, thus yielding an adsorbent of constant specific surface area (*i. e.*, surface per unit mass of adsorbent).

Effect of Aging the Hydrous Oxides on the Amount of Barium Ion Retained.—For this purpose, two sets of experiments were carried out using solutions containing 500 mg. of aluminum, chromic and ferric ions separately, 40 mg. of barium ion, 10 ml. of 0.02% gelatin solution and 1 g. of ammonium chloride. In the first set the procedure was the same as above. In the second set the solutions were allowed to age in stoppered flasks for six days before filtering, washing and determining the amount of barium in the filtrates and washings. These two sets of experiments were repeated with 4 g. of ammonium chloride. To obtain additional data on the effect of ammonium chloride on the amount of barium ion lost the first set of experiments was repeated in saturated ammonium chloride solutions. The results are shown in Table II.

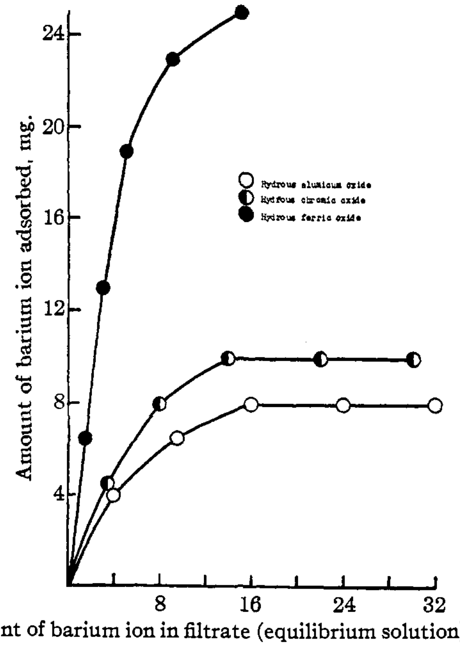

Fig. 1.—Adsorption isotherms of barium ion with hydrous aluminum, chromic and ferric oxides in the presence of 1 g. of ammonium chloride.

TABLE II

EFFECT OF AGING HYDROUS ALUMINUM, CHROMIC AND FERRIC OXIDES ON THE AMOUNT OF BARIUM ION RETAINED

Metal	NH_4Cl, g.	Days aged	Ba^{++} in filtrate, mg.	Ba^{++} lost, mg.
Al^{+++}	1	0	16	24
Al^{+++}	1	6	11	29
Al^{+++}	4	0	20	20
Al^{+++}	4	6	17	23
Al^{+++}	satd.	0	30	10
Cr^{+++}	1	0	7	33
Cr^{+++}	1	6	4	36
Cr^{+++}	4	0	10	30
Cr^{+++}	4	6	7	33
Cr^{+++}	satd.	0	29	11
Fe^{+++}	1	0	4	36
Fe^{+++}	1	6	11	29
Fe^{+++}	4	0	11	29
Fe^{+++}	4	6	18	22
Fe^{+++}	satd.	0	28	12

It is seen that aging decreases the amount of barium retained by hydrous ferric oxide while the opposite effect is shown with hydrous aluminum and chromic oxides. Increasing the amount of ammonium chloride reduces the loss of barium ion. This effect is slightly different for each hydrous oxide but practically the same whether they are aged or not.

Effect of Adding the Barium Ion, after the Formation of the Hydrous Oxides, on the Amount Lost.—Two sets of

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(8) Curtman, "Qualitative Chemical Analysis," revised edition; The Macmillan Co., New York, N. Y., 1938, p. 298.

experiments were performed. For the first set, solutions were made consisting of mixtures of equal amounts of aluminum and chromic ion, because of their similar action as shown in the previous experiments, varying from 15–250 mg. each, 40 mg. of barium ion, 10 ml. of 0.02% gelatin and 1 and 4 g. of ammonium chloride. The hydrous oxides were precipitated with ammonia as in the experiments above and the amount of barium in the filtrates and washings determined. In the second set the barium ion was added immediately after precipitation and then the amount in the filtrates and washings determined. For the purpose of noting the action of hydrous ferric oxide, the second set of experiments was repeated with 500 mg. of ferric ion. The results are shown in Table III.

TABLE III

EFFECT OF ADDING BARIUM ION, AFTER PRECIPITATION OF THE HYDROUS OXIDES, ON THE AMOUNT LOST

Mg. of metal	NH_4Cl, g.	Ba^{++}, when added	Ba^{++} in filtrate, mg.	Ba^{++} lost, mg.
500 Al^{+++} and Cr^{+++}	1	Before	19	21
500 Al^{+++} and Cr^{+++}	1	After	23	17
500 Al^{+++} and Cr^{+++}	4	Before	28	12
500 Al^{+++} and Cr^{+++}	4	After	30	10
200 Al^{+++} and Cr^{+++}	1	Before	21	19
200 Al^{+++} and Cr^{+++}	1	After	25	15
200 Al^{+++} and Cr^{+++}	4	Before	29	11
200 Al^{+++} and Cr^{+++}	4	After	30	10
50 Al^{+++} and Cr^{+++}	1	Before	35	5
50 Al^{+++} and Cr^{+++}	1	After	36	4
30 Al^{+++} and Cr^{+++}	1	Before	37	3
30 Al^{+++} and Cr^{+++}	1	After	37.5	2.5
500 Fe^{+++}	1	After	8	32
500 Fe^{+++}	4	After	14	26

In every case there is less barium ion retained (lost) if it is added after precipitation than if present in the original solution. However, it is seen that in similar experiments nearly as much barium ion is lost with 500 mg. of precipitate as with 200 mg. While adsorption is probably taking place, yet different amounts of adsorbent are being formed in the same volume (25 ml.). Thus it cannot be assumed that the conditions of the precipitation process are the same. Specific surface areas, therefore, might not be constant and the same conditions as to saturation would not result. Unfortunately the purpose of this work was to study the problem as it arises from the use of an accepted analytical method. Later, in the discussion, possible explanations will be given of these unusual results.

Combined Effect of Aging the Mixed Hydrous Aluminum and Chromic Oxides and the Addition of Barium Ion at Different Times on the Amount Retained.—Four sets of experiments were carried out. Solutions containing mixtures of 100 and 250 mg. each of aluminum and chromic ions, 10 ml. of 0.02% gelatin and 1 and 4 g. of ammonium chloride were prepared. In the first set 40 mg. of barium ion was added to the solutions, the hydrous oxides precipitated with concentrated ammonia as usual and the solutions allowed to age six days in stoppered flasks. Then the solutions were filtered, the precipitates washed free of barium ion, the filtrates and washings evaporated and the amount of barium ion determined. In the second set the procedure was repeated, only the 40 mg. of barium ion was added immediately after precipitation and then the solutions allowed to age six days in stoppered flasks. The third set duplicated the procedure except that the 40 mg. of barium ion was added after the hydrous oxides had aged for six days in stoppered flasks and then the solutions were filtered. In the last set the previous procedure was repeated with the addition of allowing the solutions to re-age two days in stoppered flasks after the 40 mg. of barium had been added. Table IV shows the results obtained.

TABLE IV

COMBINED EFFECT OF AGING THE HYDROUS OXIDES AND THE ADDITION OF BARIUM ION AT DIFFERENT TIMES ON THE AMOUNT RETAINED

Mg. of metal	Amount of NH_4Cl	When Ba^{++} was added	Ba^{++} in filtrate, mg.	Ba^{++} lost, mg.
500 Al^{+++} and Cr^{+++}	1	Before pptn., before aging	11	29
500 Al^{+++} and Cr^{+++}	1	After pptn., before aging	21	19
500 Al^{+++} and Cr^{+++}	1	After aging	26	14
500 Al^{+++} and Cr^{+++}	1	After aging, before reaging	27	13
500 Al^{+++} and Cr^{+++}	4	Before pptn., before aging	23	17
500 Al^{+++} and Cr^{+++}	4	After pptn., before aging	25	15
500 Al^{+++} and Cr^{+++}	4	After aging	28	12
500 Al^{+++} and Cr^{+++}	4	After aging, before reaging	35	5
200 Al^{+++} and Cr^{+++}	1	Before pptn., before aging	17	23
200 Al^{+++} and Cr^{+++}	1	After pptn., before aging	23	17
200 Al^{+++} and Cr^{+++}	1	After aging	28	12
200 Al^{+++} and Cr^{+++}	1	After aging, before reaging	33	7
200 Al^{+++} and Cr^{+++}	4	Before pptn., before aging	25	15
200 Al^{+++} and Cr^{+++}	4	After pptn., before aging	28	12
200 Al^{+++} and Cr^{+++}	4	After aging	33	7
200 Al^{+++} and Cr^{+++}	4	After aging, before reaging	37	3

A study of the results, especially when compared with those in previous tables, yields certain information. The same conclusion obtained from the data in Table III, *viz*,. less barium ion is lost if it is added after precipitation than if present in the original solution, also holds here. On comparing the results of this Table with similar experiments in Table III it is seen that aging the hydrous oxides in the presence of barium ion increases the amount retained (lost). Apparently, however, the loss from aging must be due to more than one factor as reaging results in a decrease of this loss. The anomalous behavior, *i. e.*, nearly the same loss of barium ion with 500 mg. of precipitate as with 200 mg., noted in connection with Table III, is also seen here.

Discussion

From the results of the first experiments it is evident that the loss of barium ion is not due to its precipitation as a carbonate, brought on by the absorption of carbon dioxide, contrary to Zolotukhin's assertion.[9] Yet, in later experiments, a definite amount of barium ion is lost where solutions containing precipitated hydrous oxides are kept in stoppered flasks. It is interesting to note in this connection that Curtman and Frankel, in determining the loss of barium ion due to the absorption of carbon dioxide by ammonia, said,

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(9) Ref. 2b.

"Contrary to expectations, the loss in this operation was far greater than one might think."[10]

From the nature of the hydrous oxides and the fact that Fig. 1 is a typical Freundlich isotherm, the loss of barium ion is probably due to adsorption. In every experiment carried out, as the amount of ammonium salt present was increased, less barium was lost. Evidently ammonium ion replaces barium in the adsorption. This is in agreement with results reported by others.[6] This explains why Zolotukhin found that on washing the hydrous oxides with solutions of ammonium salts less barium ion was lost. In a saturated solution of ammonium salts some barium ion is still not recovered. This might be due to an incomplete replacement of barium by ammonium ion in the adsorption or else to occlusion of cations by the hydrous oxides as they are being formed. Increasing the amount of ammonium ion has a similar action, though different in extent, on the decrease of the loss of barium ion for each of the hydrous oxides. Yet in a saturated solution of ammonium ion, all three hydrous oxides, separately, adsorb about the same amount of barium ion. Important in analysis is the fact that while a high concentration of ammonium ion will decrease the adsorption of barium ion, it will not allow for its complete recovery. If the loss is due to surface adsorption, then it will be the same whether the barium ion is present before the hydrous oxides are precipitated or added immediately after. The results in Table III show there is a difference in the amount of barium ion lost depending on whether it is present before or after the precipitation. This indicates that besides surface adsorption some other effect must be occurring.

It already has been mentioned in connection with Tables III and IV that certain results appear to be anomalous. From Table I and Fig. 1 the surfaces of the precipitates of hydrous aluminum and chromic oxides are saturated when there is 14 mg. and 16 mg., respectively, or more barium ion in the filtrate. Besides there is a constant ratio of the amount of barium ion adsorbed to the amount of adsorbent when saturated. Therefore, in Table III, in similar experiments where 30, 50 and 200 mg. of mixed aluminum and chromic ion is precipitated in the presence of barium ion, the surfaces of the precipitates are saturated. Not only is there more than the criterion amount of barium ion in the filtrate, but there is a constant ratio of 1 mg. of barium ion retained to 10 mg. of mixed hydrous oxides. In the similar experiments where the barium ion was added after the precipitation, in order to eliminate occlusion, a slightly lower ratio, as is to be expected, of about 1:12 is obtained. But in the case of the experiments using 500 mg. of aluminum and chromic ion, the amount of barium ion retained is too low for saturation and therefore the amount in the filtrate is too high. It would seem, for some reason not apparent, that the surfaces of the precipitates in the latter are *not* saturated with barium ion. With a large amount of precipitate it might take a longer time before saturation is reached,[11] or internal surfaces do not come in contact with barium ion.[12]

If occlusion takes place while the precipitate is forming, then the amount of barium lost would be less if it is added after the hydrous oxides are formed. That this effect is present can be seen from the results in Table III. Furthermore, aging the precipitate should reduce the amount of barium occluded,[13] provided there is no post precipitation. If there is, then aging the precipitates would increase the amount of barium ion lost. Thus it is seen that while all three hydrous oxides cause loss of some barium ion by occlusion, there is postprecipitation with only hydrous aluminum and chromic oxides (see Table II). That the latter effect is appreciable is shown by the larger loss of barium ion on aging, which would tend to undo occlusion at the same time and therefore decrease the amount of barium ion lost. When hydrous aluminum and chromic oxides age, some change takes place which affects postprecipitation negatively. This is seen from the reaging experiments in Table IV where less barium ion is lost if it is added to aged hydrous oxides and then aged again. Some experiments were repeated in which the hydrous oxides were aged in the presence of barium ion for two days instead of six. The same results were obtained for the amount of barium ion lost, showing the postprecipitation was complete within two days.

Summary

1. The loss of barium ion when hydrous aluminum, chromic and ferric oxides are pre-

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[10] Ref. 1, p. 728.

[11] Kolthoff and Stenger, *J. Phys. Chem.*, **36**, 2113 (1932).

[12] (a) Reference (11); (b) Kolthoff and Overholser, *ibid.*, **43**, 778 (1939).

[13] Reference 4(c), page 881.

cipitated by ammonia in the presence of ammonium salts is not due to the formation of barium carbonate by absorption of carbon dioxide.

2. The loss of barium ion when hydrous aluminum, chromic and ferric oxides are precipitated by ammonia in the presence of ammonium salts is probably due partly to surface adsorption.

3. Ammonium ion replaces barium in the adsorption, yet all the barium ion is not recovered even in a saturated solution of ammonium salts.

4. All three hydrous oxides cause the loss during precipitation of some barium ion by occlusion.

5. Hydrous aluminum and chromic oxides also cause the loss of some barium ion by postprecipitation.

6. When large amounts of hydrous oxides are precipitated, the surfaces do not become saturated with barium ion.

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Equilibrium in an Esterification Reaction with Perchloric Acid as Catalyst

BY H. M. TRIMBLE AND EARL L. RICHARDSON

Many workers have found that the equilibrium concentrations in reversible homogeneous reactions change when a catalyst is introduced, and that the degree of change varies with the concentration of the catalyst. Few, however, have investigated the phenomenon with other than small concentrations of the catalyst. This paper reports the results of a study of the reaction

$$CH_3COOH + C_2H_5OH \rightleftarrows CH_3COOC_2H_5 + H_2O$$

in the presence of perchloric acid over a wide range of concentration. The efficiency of this substance in promoting simple esterification has not been examined previously, so far as the authors have been able to determine.

Experimental

Reagent grade perchloric acid, 70%, conforming to A. C. S. specifications was redistilled. It was diluted as needed to give aqueous solutions varying from 0.37 to 71.2% perchloric acid by weight which were used in making up the different reaction mixtures. Reagent grade glacial acetic acid was redistilled, saving the middle 75%. Repeated analyses showed it to be 99.8% pure. Ethyl alcohol was freed from aldehydes by treating it with silver oxide as described by Dunlap[1] and distilling. Its density was determined at 30° several times during the course of the work and found to remain constant at 0.80056 ± 0.00004. Reference to the tables by Osborne[2] shows that it contained 93.2% C_2H_5OH. The base used in all the titrations was approximately half normal sodium hydroxide. It contained a small excess of barium chloride, and it was protected at all times with soda lime tubes to ensure the absence of carbonate. It was standardized by means of reagent grade potassium hydrogen phthalate with phenolphthalein as indicator.

The experiments were run at 30.00 ± 0.05°. The reaction vessels were 100- or 250-ml. bottles with well-fitting ground-glass stoppers. In experiments 1 to 7, 10-ml. portions of perchloric acid solution and 2-ml. portions each of acetic acid and ethyl alcohol, all measured at 30° by means of precision pipets, were taken in making up the reaction mixtures; in the other experiments half these quantities were used. The stoppers were sealed externally with paraffin wax and the bottles were immersed in the bath for three days or longer to allow the reaction to proceed to equilibrium. Titrations of the total acid present at equilibrium were carried out rapidly in the reaction vessels after adding ice water. Each experiment was run in triplicate, and repeated if the results failed to check satisfactorily. Portions of the perchloric acid solution used for each experiment were weighed and titrated at the same time as the mixture itself. The quantities of the organic substances delivered were checked by weighing, and found

TABLE I

EQUILIBRIUM DATA AND RESULTS

Expt.	$HClO_4$ soln., *m*	$HClO_4$	H_2O	EtOAc	*M* Mole % $HClO_4$	K^a apparent
1	0.038	0.00038	0.5636	0.00476	0.06	3.32
2	.066	.00066	.5634	.00492	.11	3.47
3	.097	.00096	.5612	.00498	.15	3.51
4	.144	.00142	.5608	.00513	.23	3.65
5	.342	.00335	.5561	.00530	.54	3.79
6	.733	.00707	.5482	.00576	1.15	4.19
7	.92	.00876	.5438	.00600	1.57	4.41
8	1.37	.00647	.2695	.00329	2.11	5.00
9	2.26	.01033	.2615	.00364	3.43	5.67
10	3.04	.01347	.2533	.00407	4.55	6.57
11	3.77	.01628	.2480	.00436	5.55	7.22
12	4.29	.01822	.2440	.00458	6.26	7.74
13	4.73	.01946	.2370	.00485	6.83	8.33
14	6.15	.02432	.2284	.00528	8.66	9.42
15	8.02	.02989	.2165	.00583	10.92	10.88
16	9.26	.03288	.2067	.00610	12.32	11.45
17	12.79	.04090	.1890	.00664	15.94	12.67
18	15.93	.04706	.1745	.00693	18.98	12.95
19	19.01	.05201	.1627	.00718	21.60	13.19
20	24.61	.05924	.1448	.00760	25.79	13.51

[a] $K_{apparent}$ = moles EtOAc × moles H_2O/moles AcOH × moles EtOH.

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[1] Dunlap, THIS JOURNAL, **28**, 397 (1906).

[2] Osborne, *Bull. Bureau Standards*, **9**, 424–425 (1913).