

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WASHINGTON]

THE ADSORPTION OF SILVER NITRATE BY FINELY DIVIDED SILVER

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There have been only a limited number of investigations showing the adsorption by a metal of its salts from aqueous solution. Patrick and Bachman¹ and Rosenberg and Stegeman² have studied the adsorption by mercury of the ions from solutions of mercuric salts. The most outstanding results are those reported by Euler and his co-workers³ on the adsorption of silver nitrate by finely divided silver and silver foil. They report adsorption varying from 7.5 to 27.3% depending on the area of the silver surface and the concentration of the solution.

If silver adsorbs its salts to this degree, the potential of the silver electrode should be in part an adsorption potential. Furthermore, the potential of silver against its solution containing its ions would probably be very unsteady, and be influenced by the presence of gases such as oxygen.⁴ But Lewis⁵ has found the potential quite steady. He states, however, that plate silver has a more negative potential than silver in the finely divided state. The potential of the plate silver was more subject to change. One would be justified in the inference that these small differences might be due to adsorption of ions from solution.

The object of this investigation was the verification of the work of Euler and Hedelius. It was also contemplated, if marked adsorption occurred, to study the influence of gases such as oxygen, nitrogen, etc.

Experimental Part

Preparation of Solutions.—All silver solutions were kept in carefully cleaned Pyrex bottles. In order to protect the solutions from the action of light, the bottles were covered with black, rubberized cloth and were kept in the dark. Such work as recrystallization, transfer of solutions, precipitation, evaporation, etc., was carried out in the presence of light only sufficient to permit experimental manipulation.

The silver nitrate used was a commercial "C. P. Analyzed" product which was recrystallized once and dried under reduced pressure at room temperature. Eight solutions were prepared varying in approximate normality from 0.1 to 0.0001. The quantitative analysis of these solutions is given with the adsorption experiments reported in Table I.

Solutions 1 and 2 were analyzed volumetrically with a solution of ammonium thio-

¹ Patrick and Bachman, *J. Phys. Chem.*, **30**, 134 (1926).

² Rosenberg and Stegeman, *ibid.*, **30**, 1306 (1926).

³ Euler and Hedelius, *Arkiv. Kemi, Mineral. Geol.*, **7**, No. 31, 1716 (1920); Euler, *Z. Elektrochem.*, **28**, 446 (1922).

⁴ Tartar and McClain, *THIS JOURNAL*, **53**, 3201 (1931).

⁵ Lewis, *ibid.*, **28**, 158 (1906).

cyanate which had been carefully standardized by the use of recrystallized silver nitrate, c. p. silver wire, and pure electrolytic silver. Solutions 3, 5, 6 and 8 were analyzed gravimetrically.⁶ For the analysis of solution 8, the most dilute, a 1000-cc. portion was required.

Preparation of Finely Divided Silver.—Silver was prepared by three different methods.

In the first method, silver carbonate was precipitated by adding sodium carbonate to a solution of silver nitrate. The precipitate was washed approximately thirty times with distilled water, dried at room temperature and reduced to silver in an atmosphere of hydrogen with very gentle heating. The product was analyzed volumetrically and found to be pure silver within the limits of experimental error.

This method is essentially the same as that used by Lewis⁵ for the preparation of silver in the determination of the potential of the silver electrode.

The second method of preparation was that employed by Euler and Hedelius³ in their experiments on adsorption by metallic powders. Precautions were taken to reproduce as nearly as possible this method of preparing silver in finely divided form. Silver chloride was prepared from silver nitrate and the former reduced by zinc under water. The excess zinc was then removed by treatment and decantation of a 10% sodium hydroxide solution. Each treatment with this solution was followed by three to four and sometimes ten to twelve decantations with water. It was necessary to extend this process over a week, involving sixteen treatments with sodium hydroxide. After the last treatment with sodium hydroxide, the product was thoroughly washed with water. The silver met the requirements of the qualitative test for purity suggested by Euler and Hedelius. A one-gram sample was first dissolved in nitric acid, the absence of a turbidity showing that no chloride was present. The silver was then precipitated as the chloride by adding hydrochloric acid and filtered. Sodium carbonate was added in slight excess to the filtrate. The absence of a turbidity after several hours' standing was assumed to indicate that the silver was zinc-free.

The third method was that used by Richards and Wells.⁷ Ammonia gas was passed into 40–50 cc. of a freshly distilled formic acid. The acid was kept cool in an ice-bath to aid the formation of ammonium formate. The solution, which was distinctly acid, was then heated and 100 cc. of a solution containing 25 g. of silver nitrate was poured in slowly with stirring. Metallic silver was rapidly produced and was much finer and more spongy than that produced by the other two methods. It was washed about thirty times with water by decantation and dried at room temperature under reduced pressure. Careful analysis showed the metal to be pure within the limits of experimental error.

Determination of Adsorption.—The method for determining adsorption was carried out as follows. A carefully measured portion of silver nitrate solution was transferred to a Pyrex bottle containing a weighed amount of sponge silver. The mixture was well shaken and placed in a thermostat at 25° overnight. The silver settled easily, leaving a very clear supernatant liquid. A portion of the solution was then taken by means of a pipet and analyzed.

Dilute solutions were used in the greater portion of the experiments

⁶ Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929, p. 164. The samples were heated for a longer period and at a temperature not exceeding 100°.

⁷ Richards and Wells, *THIS JOURNAL*, 27, 475 (1905).

because any adsorption would be more apparent. The experimental data are reported in Table I.

TABLE I
RESULTS OF ADSORPTION EXPERIMENTS

Expt.	Method of prepn. of silver	Silver used, g.	Soln.	AgNO ₃ soln. for analysis, cc.	Silver soln. in contact with adsorbent, cc.	Silver in solution Before contact with adsorbent, g.	Silver in solution After contact with adsorbent, g.	Silver adsorbed g.
1	1	1.0	1	25	50	0.5395	0.5395
2	1	1.0	2	50	150	.6468	.6477	-0.0009
3	1	5.0	3	25	50	.1075	.1081	- .0006
4	1	5.0	6	150	200	.0214	.0221	- .0007
5	1	5.0	8	1000	1100	.0161	.0167	- .0006
6	2	2.0	4	50	150	.1609	.1339	+ .027
7	2	2.0	6	150	250	.0267	.0142	+ .0125
8	3	5.0	5	50	150	.0808	.0798	+ .0010

Discussion of Results.—The data show no evidence of positive adsorption of silver nitrate by the silver metal. Experiments 2, 3, 4 and 5 show a small increase in the concentration of silver nitrate, indicating negative adsorption. Experiment 8 shows a small decrease in the concentration of the silver nitrate solution, indicating positive adsorption. The changes are slight and may be entirely due to experimental error. On the other hand, experiments 6 and 7, in which silver prepared according to Euler and Hedelius³ was used, indicate marked adsorption, 16.8 and 46.8%, respectively.

The writers do not believe that this change is due to adsorption but rather to the reducing action of the small amount of zinc present. The removal of the last traces of zinc from sponge silver with 10% sodium hydroxide is difficult. Furthermore, the precipitation of zinc in alkaline solution with sodium carbonate is not a satisfactory test to establish the absence of zinc. The silver nitrate solutions obtained in experiments 6 and 7 were treated with hydrochloric acid in excess to precipitate the silver. Portions of these filtrates were tested with sodium carbonate for the presence of zinc but no precipitate formed after several days' standing. When samples of these same filtrates were treated with ammonium hydroxide and hydrogen sulfide a precipitate of zinc sulfide was formed almost immediately.

Euler³ has also reported high adsorption of silver nitrate on silver foil, but careful scrutiny of the papers indicates that the foil used was not free from metals more active than silver. In fact, the statements indicate that Euler assumed that such impurities do not seriously affect adsorption measurements.

Summary

1. A study has been made of the adsorption of silver salts by silver prepared by different methods. The results do not show positive adsorption.

2. The experimental work of Euler and Hedelius has been confirmed, but the writers present evidence to show that these results are due to the presence of zinc in the silver used.

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HEXAFLUORODISILANE¹

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The only binary fluoride of silicon that has been definitely established up to the time of the present writing is the tetrafluoride, SiF_4 . To be sure, H. St. C. Deville,² and Troost and Hautefeuille³ reported the formation of substances which they believed to be subfluorides when (a) aluminum and silicon tetrafluoride were heated; (b) the gaseous tetrafluoride was passed over hot silicon; or (c) when a spark was passed through the tetrafluoride between silicon electrodes. The supposed subfluorides were described as gaseous, liquid, and solid.

In more recent times Jacquerod and Tourpaian,⁴ working upon the density of silicon tetrafluoride, attempted to account for observed high values by the assumption that the passage of the gas over glass wool at red heat might have the effect reported by Troost and Hautefeuille, although the latter investigators passed the gas over elementary silicon at a much higher temperature. Furthermore, since no analyses either for silicon or fluorine were mentioned, and since the high densities referred to may be accounted for in several other ways, the evidence in favor of a subfluoride must be considered as based largely upon the work of the earlier experimenters.

Repetition of this work has failed to confirm the results claimed. Thus Ruff⁵ states that he failed to obtain the subfluoride, of unknown composition, either by passage of the tetrafluoride over molten silicon and rapid cooling of the vapors, or by reduction of the tetrafluoride by graphite at 2000° , or by reduction with hydrogen; and Mellor⁶ states that "the evidence for the existence of the subfluoride is not unimpeachable; and its composition is unknown."

¹ The present paper constitutes the detailed account of the work upon Si_2F_6 , referred to in our communication to the Editor published in *THIS JOURNAL*, 53, 3191 (1931).

² H. St. C. Deville, *Ann. chim. phys.*, [3] 49, 76 (1857).

³ Troost and Hautefeuille, *ibid.*, [5] 7, 464 (1876).

⁴ Jacquerod and Tourpaian, *J. chim. phys.*, 11, 19 (1913).

⁵ Ruff, "Die Chemie des Fluors," 1920, p. 119.

⁶ Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," 1925, Vol. VI, p. 934.