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ELECTRO ENDOSMOSIS AND THE PREPARATION OF SOLID ALKALI AMALGAMS.

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It was found when using the Shepherd method of making solid amalgams that increasing the current applied to a given cathode area and allowing adequate time, accelerates otherwise sluggish electro endosmotic effect with the porous cups and electrolyes used. The observations of G. McP. Smith and Bennett on the electro preparation of solid alkali amalgams were substantially confirmed in the cases tried, namely with potassium, barium, strontium and calcium. The use of low temperatures and non-aqueous electrolytes made no improvement over earlier efforts to produce solid calcium amalgam electrolytically.

The Shepherd Method of Making Solid Amalgams.—Shepherd[1] suggested an improved method of making solid amalgam by electrolysis. He supported a porous cup containing the mercury as cathode, so that the cup was submerged but slightly in the anolyte and used less than 8 volts. It had been noticed in previous work with this method[2] that electro endosmosis developed; in fact this was a difficulty in that method which

[1] *J. Phys. Chem.*, **7**, 29 (1903).

[2] G. McP. Smith and Withrow, THIS JOURNAL, **29**, 321 (1907).

had to be overcome. One of the present writers has been in the habit of utilizing this difficulty as a convenient lecture demonstration of the phenomenon of electro endosmosis, to furnish a ground work for the discussion of permeable diaphragm cells for chlorine manufacture.

Electro Endosmosis with the Shepherd Cell.—Complicated apparatus has been used customarily in the study of electro endosmosis.[1] Some of the forms of apparatus employed by these workers could be used for lecture demonstration, but they lack the directness of appeal of bare, porous-cup demonstration of the effect, such as a modification of Shepherd's porous-cup method for the preparation of solid amalgams can be made to give. The latter apparatus is simple, and expensive platinum cathodes are eliminated. Striking manipulation is made possible by beginning the demonstration with the bottom of the porous cup containing the mercury cathode submerged but a few millimeters below the level of the anolyte. Upon electrolysis for less than an hour, starting with the cathode cup entirely free of electrolyte, the endosmosed liquid will rise within the cell over the mercury several centimeters *above* the outside level of electrolyte and may be poured out of the porous cup as a visible, measurable demonstration of the electro endosmotic effect.

After considerable use of the method, unexpected failure to get any effect at all, in some trials, rendered necessary a laboratory study of the proper conditions for the Shepherd experiment as an illustration of the endosmosis phenomenon. The statements in the literature as to the essentials governing the phenomenon are vague or non-concordant. Stewart[2] says the current must be "sufficiently strong." Wiedemann,[3] states that the phenomenon is dependent on current strength and independent of the area or thickness of the diaphragm. Byers and Walter[4] state "the flow of liquid through the septum is proportional to the intensity of the current." Briggs, Pierson and Bennett[4] state "the volume of liquid transported in unit time is directly proportional to the external potential applied."

[1] Morse and Olsen, THIS JOURNAL, **23**, 437 (1900); Reed, *Trans. Am. Electrochem. Soc.*, **2**, 240 (1902); Frazer and Holmes, *ibid.*, **40**, 320 (1908); Bancroft, *Trans. Am. Electrochem. Soc.*, 21, 233 (1912); Byers and Walter, THIS JOURNAL, **36**, 2284 (1914); Taylor, "The Chemistry of Colloids," p. 66–74, New York, Longmans, Green and Co., 1915; Briggs, Pierson and Bennett, *Trans. Am. Electrochem. Soc.*, **31**, 257 (1917).

[2] "Recent Advances in Physical and Inorganic Chemistry," p. 94. Longmans, Green and Co., New York.

[3] "Text Book of Electro Chemistry," p. 157, LeBlanc, trans. Whitney and Brown, Macmillan Co., New York, 1907.

[4] *Ibid.*

Experimental.

The work in the two previous papers[1] on the porous-cup method of making solid amalgams was repeated for the purpose of observing the relationship of the electro endosmotic effect to other conditions. The results given in the following table are typical:

TABLE I.

Expt.	Electrolyte.	Mercury used. G.	Current. Amperes.	Current. Volts.	C. D. 100 amps.	Maximum temperature. Cup. °C.	Maximum temperature. Anolyte.	Time. Minutes.	Endosmosis. Mm.
1	KCl.	60	1.8–3.0	12.5–13.5	41–60	95.5	67	29	0
2	50 cc. —K_2SO_4	69	1.0–1.7	19–22	23–39	95	63	24	5
3	50 cc. —K_2SO_4	64	0.2	8	5	30	28	66	6
4	150 cc. —K_2SO_4	507	1.6–2.1	18–21	10–13	75	58	62	38
5	—K_2SO_4	196	0.3–0.35	10	1.9–2.2	32	29	70	5
6	—K_2SO_4	507	0.6–0.2	10	3.8–1.3	25	23	80	5
7	50 cc. —KCl	250	2.4–3.1	6	.....	45		56	..
8	50 cc. —KCl	250	3.0	5.5–6	.....	52		80	..
9	50 cc. —KCl	250	3.0	6	.....	55		40	..
10	50 cc. —$SrCl_2$	260	2.6–2.9	7.5–6.5	.....	45		102	..
11	35 cc. —$(CH_3CO_2)_2Ca$	150	1.3–2.5	10	.....	70		68	..

Saturated solutions were used in beginning all experiments. The porous cups holding the mercury (cathode) were immersed 0.5 to 1.0 cm. in the electrolyte. Those used in Expts. 1 to 3 were 21 mm. and those in 4 to 6 were 40 mm. in diameter. Run 1 yielded a solid crystalline amalgam and yet no endosmosis took place. The cup had been soaked in water for 24 hours previous to the experiment. Expt. 2 was suddenly terminated by the deposition of a crust of salt on the outside of the cup. The cup had been soaked an hour before starting. The amalgam was solid when poured into water at 22°. In Expt. 3 a low voltage was used to find the influence of such voltage on osmosis using nearly triple the time of Expt. 2. Solid amalgam was not produced. The cup had been soaked 45 minutes previous to the experiment. Expt. 4 duplicated the conditions and results of Smith and Withrow,[2] using a common but different make of porous cup of 4 × 8 cm. There accumulated 38 mm. of solution on top of the amalgam and it was still rising when the current was stopped, though solid amalgam was not reached. In Expts. 5 and 6 with lowered voltage using the same cup, no electro osmosed solution appeared until after 28 to 30 minutes. This showed the depressing effect on electro endosmosis of lowered voltage and the concomitantly lessened current flow. It appears from these results that the electro endosmotic effect is somewhat modified by the character of the porous cell used, but any failure to appear or any retarding action can be overcome in all the

[1] Shepherd, *loc. cit.*; and Smith and Withrow, *loc. cit.*

[2] *Ibid.*

types of cup at our disposal by raising the voltage (increasing the current density). The exact figure will vary with the individual cup, but we found steady endosmosis, using 20 to 25 volts in place of the 6 to 8 volts of Shepherd on amalgams. This conclusion is borne out by the experience recorded by Smith and Withrow,[1] who used as high as 22 volts in one case, but did not note its influence. A study of the relation between porosity and this endosmotic effect, as well as the relation of other factors, would be of further interest, but was not necessary to accomplish our object. Potassium sulfate appears to be more satisfactory than the chloride. The Shepherd mercury cathode cups appear to have advantages for the study of this phenomenon of whose bearing upon the design and operation of commercial alkali-chlorine diaphragm cells there is too little appreciation. The matter merits further study.

Lecture Demonstration of Electro Endosmosis with the Shepherd Cell.

For the Shepherd device as a lecture demonstration of electro endosmosis, one should use a good grade of porous cup about 40 × 80 mm. It should be held by a clamp so that it visibly extends one cm. or less below the level of the anolyte, preferably saturated potassium sulfate solution contained in a beaker. The whole should be supported so that heat may be applied if necessary. A layer of mercury 5 mm. deep as cathode within the porous cup is electrically connected by a platinum point protruding from the usual glass seal connection. To facilitate prompt action the cup may be soaked in a dilute solution of the electrolyte overnight prior to the demonstration. Any form of platinum anode may be used in the beaker containing the anolyte. Twenty to twenty-five volts will suffice to enforce electro endosmosis with the ordinary porous cup.

Solid Alkali-Amalgams.—In the course of the work on electro endosmosis there was opportunity for parallel runs for the electro production of solid alkali-amalgams by other methods. Examples of these are given (Expts. 7 to 11) in the above table. In all of these cases the procedure of Smith and Bennett[2] was followed.

Potassium Amalgam.—When poured into water, Expt. 7 gave a thick but not solid amalgam due to furnishing a larger area for decomposition than did Smith and Bennett. Using the same size beaker as used by them, after 10 minutes in Expt. 8, crystals of amalgam began to form on top of the mercury[3] and rapid evolution of hydrogen took place when the crystals were not constantly stirred into the mercury. Upon pouring into cold water the amalgams did not form a solid cake, but masses of fine crystals could be fished out with the fingers. The product of Expt.

[1] *Loc. cit.*

[2] THIS JOURNAL, 31, 799 (1909).

[3] *J. Phys. Chem.*, 20, 530 (1916).

9, where crystals began to form in about 15 minutes, did solidify when poured into a beaker of water surrounded by ice. The amalgam remained solid at 5°.

Strontium Amalgam.—In Expt. 10 there was a 24-minute interruption in the middle, due to cessation of current. The resulting amalgam was too thick to pour and when it was dumped into cold water it appeared solid or in a very thick semi-solid state. The cessation of the current was due to the fouling of the platinum wire by an accumulation which shut off the current.

Calcium Amalgam.—In Expt. 11 solid calcium acetate was added from time to time. After 2 or 3 minutes the solution became milky and turbid, and in 10 minutes it became black and a thick, gray mixture of calcium hydroxide and mercury was obtained as in our previous work. Repetition in a freezing mixture gave no improvement. Experiments with non-aqueous solutions such as calcium bromide in absolute ethyl alcohol, and calcium chloride in methyl alcohol,[1] all gave the same results as aqueous solutions. Patton had deposited metallic calcium on platinum electrodes from the last electrolyte but stated that the hydroxide was deposited from ethyl and amyl alcohols. The preparation of solid calcium amalgam seems to depend upon the prevention of the formation of the hydroxide which is greatly accentuated in the case of calcium, is present in the case of strontium, but practically lacking in the case of barium. It is possible that electrolysis in solutions at just about their freezing points, might give satisfaction, or below the freezing point of water in the case of organic solvents. The observations of Reed[2] and of Haber,[3] on the projection of metallic lead into the solution when aqueous sodium hydroxide is electrolized with lead electrodes would appear to have a suggestive bearing on the formation of the black mixture of metallic mercury and calcium hydroxide. The calcium amalgam attacks the electrolyte so strongly that it holds the mercury in finely divided state in the calcium hydroxide product.

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[1] H. E. Patton, *Jahrb. Elektrochem.*, 13, 429 (1903).
[2] *J. Frank. Inst.*, April, 1895.
[3] *Trans. Am. Electrochem. Soc.*, 2, 189 (1902).