THE SEPARATION OF WATER FROM ALCOHOL BY ELECTROOSMOSIS

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INTRODUCTION

At the present time there is considerable expense connected with the production of absolute alcohol. By far the largest item of this cost is the removal of the last five percent of the water present. An inexpensive method, therefore, is needed for the removal of this last small amount of water. This thesis is the result of work done in an attempt to evolve such a method.

Alcohol has been very important for many years in industry but has been chiefly used in the form of ninety five per cent alcohol. This is due to the fact that a mixture of alcohol and water has a minimum boiling point at this concentration. Therefore if the water is to be separated from the alcohol to give absolute alcohol, some chemical method is employed. This requires use of a dehydrating agent and then separation of the dehydrating agent from the alcohol.

Besides the reduction of price of the products which are now made from or with absolute ethyl alcohol, much more of the pure compound would be used if it were made practically as cheaply as the commercial grade now in common use. From the social side of the problem this is a very worthy project because the cost of the processing at present is due mostly to time and raw material expense. Therefore the lowering of the processing cost would not mean the necessity of employ-

ment readjustment.

There has been much work done in industrial research on this problem. However, as far as can be asertained at present, the method described in this thesis has never been tried before. This last statement is only a guess because the work carried on in plant research laboratories is quite secret.

The method of dehydration by electroosmosis has been used often before and several patents have been issued for practical utilization of the process. Although none of these are in use at the present time, their existance shows that the method has been considered feasible at various times.

H. A. Abramson, "Electrokinetic Phenomena", Appendix 3, Chemical Catalog Co., Inc., 1934.

Purpose

The object of this work is to study the electroosmosis of water alcohol mixtures with the ultimate purpose of separating the water from the alcohol. It was thought that under certain conditions the alcohol might migrate to the opposite electrode of the cell used from the water.

Theory

It is a well established fact that liquids in contact with solids create a juntion potential. That is, the liquid and solid become charged oppositely with respect to one another. Obviously in an electrolytic cell charged substances will tend to move toward electrodes of opposite charge. If the solid is in the form of movable particles it will migrate to the pole of opposite charge. This phenomena is called electrophoresis. If, on the other hand, the solid is fixed and can not move, the liquid will move toward the pole charged oppositely to it. This is called electroosmosis.

The kind and amount of charge that the liquid and solid assume when they are in contact depends on the liquid and the solid. Capillaries between the electrodes in a cell furnish the best means for studying this phenomena. The capillaries furnish large surface area and , since the potential of the liquid solid junction is independent of the area, the amount of charge on the substances is directly proportional to the area. Therefore the capacity of the cell is directly proportional to the area of the junction. Also the resistance of the capillaries to flow of the liquid, minimizes the effect of the hydrostatic head which may develop. The capillaries may be obtained in many ways. The simplest method is to have a single glass capillary connecting the anode and cathode solutions. The anode and cathode may be separated by a porous plate, or a chamber may be provided in the apparatus which can be packed with a loose material..All these methods have been used and the results obtained depended on the kind of solid and on the liquid in the cell.

The general studies that have been made are recorded in the form of speed to osmosis, and direction. Water goes to the negative electrode quite rapidly. Ethyl alcohol also goes to the negative electrode but much more slowly than does the water. Therefore if the mixture of the two liquids acts as a mixture, the water should be concentrated in the cathode chamber since it will migrate to this chamber faster than the alcohol.

Impurities in the liquid have been shown to affect the speed of osmosis greatly and even to change the direction. Thus thorium nitrate added to the water reverses its charge. Likewise some impurities added to alcohol reverse its charge and therefore the direction of migration. The difficulty of utilizing these facts lies in the necessity of removing the impurity after the water is removed, (if the water is removed).

Method Used

In spite of these apparent difficulties, impurities were added to the alcohol in an effort to obtain an idea as to the general action of the alcohol water mixtures. Thus it was necessary to have a source of potential which would also furnish an appreciable amount of current if some of the impurities added should be electrolytes. The apparatus used in this work was a commercial 400 volt d.c. rectifying set. It consisted of a transformer, 80 rectifying tube, condenser, and a wave equalizer. This set furnished a constant voltage up to a current withdrawal of 100 milliamperes and was operated on 110 volt a.c.. A 0 to 50 milliampere ammeter was connected in the circuit

The first cells tried were simple glass capillaries, made by drawing a small test tube to a capillary in the center and blowing the closed end of the tube open. The tubes were then fitted with corks containing right angle bent glass tubes and having an electrode of copper sticking through them. When assembled and filled with the liquid being tested, a flow of liquid through the capillary could be detected by change in the level of liquid in the small glass tubes. Figure 1 shows one

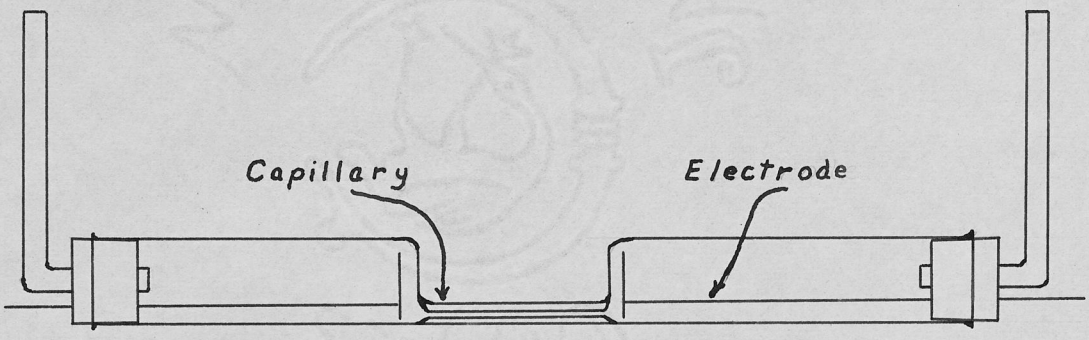


Figure 1.

of these cells. They were made with the capillary size varying greatly. But the flow through them was either too slow to be sure that there was any electroosmosis, or the flow due to hydrostatic head developed counteracted the osmotic flow.

The next type of cell used was simply a glass tube (made from a small test tube) into which a diaphragm of glass wool was forced. The wool was compressed as tightly as possible into a plug about three fourths of an inch long. The ends of the tube were closed exactly as in the apparatus described above.

No apparent osmosis was obtained when this cell was used.

The cell finally devised which gave acceptable results is shown in Figure 2.

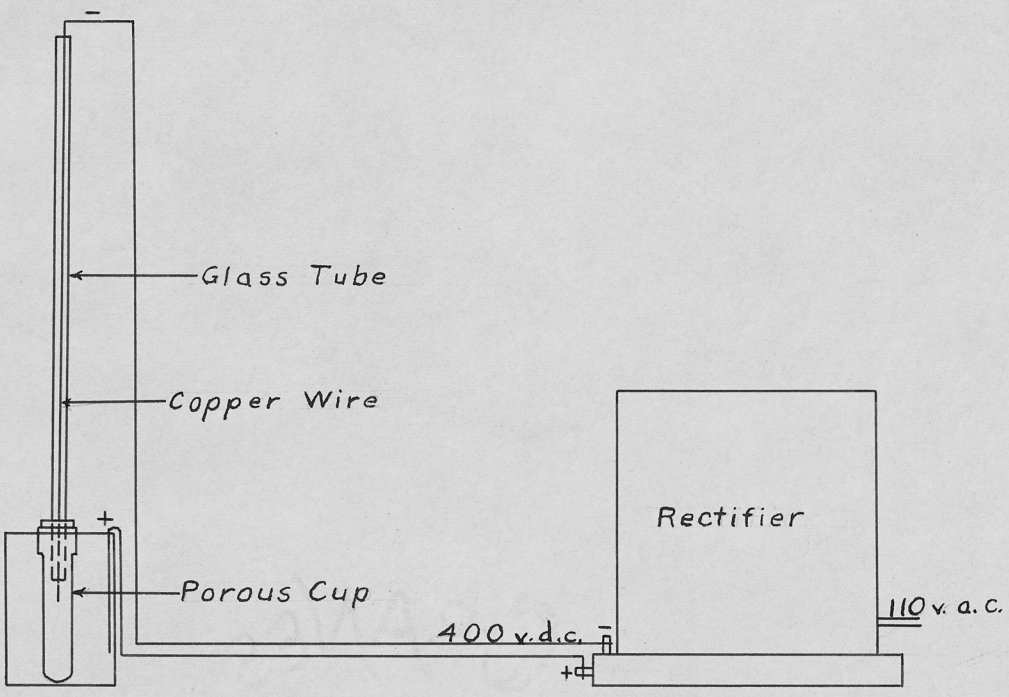


Figure 2.

This cell consists of a small glass tumbler, a porous clay cup, a long piece of 7 mm. glass tubing, and copper electrodes as shown in the drawing.

In a cell of this type the surface of the pores of the cup is the solid part of the junction. This remains unchanged when it is used. Therefore comparative results may be obtained with different liquids.

It is very difficult to keep such a cell free from impurities due to the impossibility of washing the cup completely. However, the milliammeter will show whether there is an appreciable amount of electrolyte in the solution. Likewise, when the solution in the cell is changed, some of the old will be retained in the pores of the cup and will adulterate the new solution. Since, in the work done, there was no need to know the exact ratio of alcohol to water, this made little difference.

One very probable source of error was overlooked until the work had been finished. This was the distance between electrodes. No attention was paid to the position of the cup in the tumbler and so the distance between the electrodes ranged from about three to five centimeters. This probably caused the failure to check many of the results.

Observations.

Speed of electroosmosis is measured by the speed of the rise of liquid in the vertical tube. There was only a slight amount of electrolysis at all times. The electrolysis was always evidenced by gas evolution at the negative pole.

Starting with absolute alcohol the speed of electroosmosis of alcohol water mixes was determined. The speed increased as the dilution increased, and the conductivity also increased. This was due to the conductivity of the water. However, the current never became greater than four milliamperes. In all these tests there was no appreciable separation of the solution being used.

A few liquids which are only slightly soluble in water but soluble in alcohol were added as impurities to the solution. The results showed that benzene increased the speed of osmosis, carbon tetrachloride had very little if any effect, and chloroform slowed the osmosis considerably. The chloroform apparently decomposed somewhat to give an acid reaction with the copper. The copper was deposited in a black gum on the cup. The gum contained no carbon, but had a high copper content. There was a white deposit on the positive electrode near the surface of the liquid and a light brown deposit lower. But these were in too small quantities to analyse.

The cup was cleaned by treating with dilute sulfuric acid but when this left a dark color the cleaning was finished with

aqua regia. It was very difficult to clean the cup after this treatment, for an appreciable amount of electrolyte was left in the pores. The cup was washed with distilled water until it showed very little conductivity when used in the cell with water.

After this cleaning, the cell seemed to be very materially changed. Water showed no tendency to osmose thru it. A little 95% alcohol was poured into the cup and the outside of the cell filled with the alcohol. This solution was allowed to electro-osmose for about an hour. At that time the tube had over-flowed. The liquid inside the cup was found to have a density corresponding to 81.5% alcohol, while the outer solution appeared to be 88% alcohol. Since the initial solution was much more concentrated than either of the final solutions, there must have been some decomposition. There was a deposit on the cup which appeared to be a copper salt in that it was light green and the light brown deposit appeared on the positive electrode.

Apparently the subjection to current changes the liquid so that its speed of electroosmosis is increased. The first time a solution is used it osmoses much more slowly than in later tests.

CONCLUSIONS

Under most conditions, water and alcohol mixtures act as a single compound. Thus the speed of osmosis of each when in the presence of the other is not independent of the other. Foreign substances cause a still further change in the speed of osmosis but do not change the action of the mixture so that it operates as its separate components.

With the correct solid for the capillaries, a separation can be obtained. But the alcohol is contaminated in the process.

The current or potential is too high to be used with ethyl alcohol. However, the method is shown to be feasible if used to separate mixtures which can not be decomposed by the potential used. Also if a cell can be devised which uses small enough potential not to affect the alcohol, there is still a possibility of separating the alcohol and water by this method. It can not be said on the basis of the results obtained that this separation is positive because the separation may have been catalysed by the decomposition products of the alcohol.

In brief, the conclusions are:

(1) Separation is possible, but

(2) The alcohol is decomposed somewhat, therefore

(3) The method, as used, is not practical.

BIBLIOGRAPHY

H. A. Abramsom, "Electrokinetic Phenomena", Chemical Catalog Co. Inc., 1934

Malcolm Dole, "Experimental and Theoretical Electrochemistry", McGraw-Hill Book Co., 1935.

DATA

Substance	Speed in. per min.	Current milliamps.	Remarks
Water	2.8	6	
Absolute alcohol	1.1	1	
95% "	1.9	1.5	
87% "	2.2	2	
79% "	2.9	3	impurities began
79% "	2.8	3	to appear
79% "	2.7	2.5	
79% "			
plus 1% benzene	3.7	3.2	
---	---	---	---
76% alcohol	.8	1	fresh solution
" "	1.7	1.5	No difference in density across cup.
70% "	4.3	3.5	
" "	4.1	3	
65% "	4.6	5	
" "	4.2	5	
	4.6	5	
" "	Cup filled by osmosis		No difference in density across cup.
" "			
plus 2.5% CCl_4	2.0	3	
" "	4.3	7	No difference in density across cup.

DATA

Substance	Speed in./min.	Current milliamps.	Remarks
50% alcohol	1.1	3	Fresh solution
" "	2.5	5	Decided discoloration of cup.
" "	2.1	5	
" "	3.0	5	
" "			
plus 5% $CHCl_3$	1.5	6.5	No odor of chloroform on inside.
" "	Cup filled by osmosis. Heavy deposit on cup. No difference in density.		

After cleaning cup with sulfuric acid and aqua regia, and washing thoroughly, water appeared not to osmose.

95% alcohol was put outside and cup filled by electroosmosis.

Sp. Gr. of outer solution (.8213) was equivalent to 87% alc.

" " " inner " (.8363) " " " 81.5% ".

" " " initial " (.8060)

There was an appreciable deposit on the outside of the cup.

APPROVAL

The foregoing thesis is hereby approved as a creditable study of an engineering subject, carried out and presented in a manner sufficiently satisfactory to warrant its acceptance as a prerequsite to the degree for which it has been submitted. It is to be understood that by this approval the undersigned does not necessarily endorse or approve any statement made, opinions expressed, or conclusions drawn therein, but approves the thesis only for the purpose for which it is submitted.

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