rate to a small volume and chill. The precipitated amide was filtered, washed with a small amount of alcohol and then with ether and dried. Crystallization from alcohol did not change the melting points.

The following table indicates the substituted amides that have been prepared, together with melting points, nitrogen analyses and approximate yields based on the ester.

N-SUBSTITUTED AMIDES OF SULFONE-BIS-ACETIC ACID
$SO_2(CH_2CONHR)_2$

Amine	M. p., °C.	Yield, %	N, % Calcd.	N, % Found
Methyl	186	85	13.45	13.45
Ethyl	178	78	11.86	11.57
n-Propyl	184	85	10.60	10.52
Isopropyl	148	50	10.60	10.80
n-Butyl	192	80	9.58	9.50
Isobutyl	155	65	9.58	9.60
n-Amyl	174	80	8.74	8.75
Isoamyl	152	80	8.74	8.90
n-Heptyl	182	95	7.44	7.40
Cyclohexyl	170	40	8.13	8.09

Summary

1. Ten substituted amides of sulfone-bis-acetic acid have been prepared by the interaction of the ester with primary aliphatic amines.

2. These reactions go quickly, the amides are formed in good yields and in pure condition, and appear to be convenient derivatives for the identification of these amines.

3. No reaction could be obtained under similar or more drastic conditions with 2-aminobutane, dimethylamine, diethylamine or di-*n*-propylamine.

NORMAN, OKLAHOMA RECEIVED JULY 3, 1933

Concerning Selectivity as Exhibited by Certain Osmotic Diaphragms

BY LAURIE L. BURGESS

In the course of his experience with alginic acid and products arising from it, the author observed that osmotic diaphragms could be prepared by precipitating a solution of sodium alginate with a solution of a suitable metallic salt, such as a salt of calcium, aluminum, zinc, etc. This precipitate was a colloidal jelly-like mass, which during filtration formed a continuous layer over the surface of the cloth or other medium used as a filter. When such a layer had formed, it appeared to be semi-permeable, and generally behaved like an osmotic diaphragm, so that unless this membrane was broken up by stirring, the further course of the filtration was extremely slow.

It was further observed, when a solution of complex ionic composition, such as sea water, was used to effect the precipitation of the alginate, that the filtrate appeared to show differences in the concentrations of some of its ionic constituents as compared to those in the original solution. In this particular case, the concentration of potassium in the filtrate appeared to be noticeably greater than its concentration in the original sea water. This casual observation seemed to be worthy of more extensive investigation, the results of which are embodied in this article.

The establishment of a selective action by the agency of such diaphragms would have interesting chemical and probably biological significance. Some of the marine algae, particularly the Valoniaceae, accumulate potassium chloride in preference to other salts present in the sea water. The mechanism of this accumulation has been studied extensively by Osterhout and his co-workers, who have built up an interesting theory with respect to it.[1]

Using the methods suggested earlier in this paper, it would not of course be possible to prepare diaphragms which would duplicate the performance of the living plasma membranes. Nevertheless, a study of their behavior, since they accomplish a somewhat similar result, might yield information of value in dealing with the chemical aspects of this biological problem.

Purpose of this Investigation.—The present investigation was undertaken for the purpose of determining whether or not osmotic diaphragms prepared from alginates and other materials did exert a selective action upon the substances dissolved in the solutions bathing them, and, if so, to learn which ions were favored, which were retarded and which were unaffected. It was also hoped that some further light on the theoretical explanation of selectivity might be secured.

Apparatus.—The apparatus consisted of a wooden ring, 1.3 cm. thick, with an inner diameter of 11.4 cm., and an outer diameter of 14 cm., through which two holes had been bored, as shown in the diagram, Fig. 1. The wood

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[1] For a list of papers up to 1931, see Osterhout, *Biol. Reviews*, **6**, 369 (1931). Also see Osterhout and Stanley, *J. Gen. Physiol.*, **15**, 667 (1932); Osterhout, *ibid.*, **16**, 157, 529 (1933).

was impregnated by immersion in a bath of hot paraffin. The two sides were covered with heavy canvas which was tacked to the edges of the wooden ring, and the junction was made water-tight by rotating the ring through a bath of molten paraffin. Glass tubes were passed through the two holes, as shown in the diagram, that which served as the inlet passing to the bottom of the ring, while the outlet passed barely through the wood.

In order to prepare the diaphragms, the inlet tube was connected by means of a siphon to a reservoir containing the alginate or other solution, and the solution allowed to run through the cell until the cloths were thoroughly impregnated with it. The cell was then emptied and precipitating solution run through in a similar fashion. By repeating these operations several times, a satisfactory diaphragm was built up at the inner surface and in the interstices of the cloth.

In operation, the solution to be investigated was run slowly through the apparatus, and the overflow collected in a suitable receiver. Water passed through the diaphragm, carrying with it dissolved salts by osmosis. This solution was allowed to drip away and was collected in a suitable vessel. Obviously, any number of these units could be connected in series and the solution run through the train of cells. The original solution was called the feed solution; that which passed through the apparatus and was collected at the outlet was called the overflow; while that which passed through the diaphragms and dripped away was called the drip solution. In carrying out these experiments, it was necessary for the cells to be kept full and the cloths distended at all times. If a cell became partially emptied and the cloth walls collapsed toward the center, leaks in the diaphragms were developed.

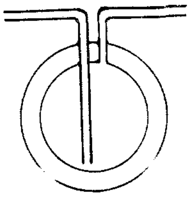

Fig. 1.

Diaphragm Materials.—Three different materials were used in preparing the diaphragms: (1) sodium alginate, (2) soap, (3) casein dissolved with sodium carbonate. In each case, solutions containing 2 to 3% of the particular diaphragm material were employed. The sodium alginate was obtained by extracting freshly gathered kelp[2] with sodium carbonate, filtering out the insoluble material and precipitating the alginic acid with hydrochloric or sulfuric acid. It was then filtered and washed thoroughly. Purification was effected by redissolving in sodium carbonate, and again precipitating with acid. This process was repeated a third time, when a jelly-like, yellowish-white material was secured, which appeared to be free from organic impurities. A sample was then dried, to determine its solid content, and the solution prepared by adding a weight of sodium carbonate equal to that of the dry alginic acid, and sufficient distilled water to produce a 2.5% solution, based on the weight of dry alginic acid.

The soap solution was prepared by dissolving Ivory soap in sufficient distilled water to yield a 3% solution.

For the casein solution, commercial casein and an equal weight of sodium carbonate were heated on the steam-bath with sufficient distilled water to yield a 3% solution. After the reaction was completed, the solution was filtered through a double thickness of cheesecloth.

A portion of the solution to be investigated was used to precipitate the diaphragm material on the cloth, and after this operation was completed, the excess was drained away as completely as possible before the cell was put into operation.

Solutions Investigated.—The solutions were either natural sea water or a synthetic solution of approximately the same composition. Those constituents of natural sea water which were present in only minute amounts were omitted from the synthetic solutions prepared from sodium chloride, sodium bromide, potassium chloride, calcium chloride, magnesium chloride and magnesium sulfate. Experiments were also made with "bittern" solutions containing the same salts and approximating the composition of the "bittern" solutions obtained when sea water is evaporated by solar heat for the manufacture of sodium chloride.

Procedure and Analytical Methods.—In each experiment, a measured volume of the feed solution was run slowly through the apparatus and the volume of the overflow and drip solutions measured. An analysis of each of these solutions was then made for the constituents which it was desired to investigate. The usual analytical methods were employed for the determination of calcium, magnesium and sulfate. For the estimation of chloride and bromide, the combined silver chloride and bromide was first weighed, and was then heated in a current of dry chlorine until it just began to fuse, and then weighed again. From the loss in weight, the chloride and bromide could be calculated.

For the determination of sodium and potassium, a measured volume of the solution was first treated with barium chloride to remove the sulfate; the excess of barium was then removed by precipitation with ammonium carbonate, which also precipitated the calcium, and the magnesium was removed by the Schaffgottsche procedure. After igniting off the ammonium salts the combined sodium and potassium chlorides were weighed. The potassium was then estimated by the perchlorate method and the sodium chloride by difference.

Obviously, the sum of the total amount in the drip and overflow should equal that in the feed solution for each constituent. This was never exactly the case, since there was a tendency for some of the salts to crystallize around the edges of the cells, which could not be washed down without altering the volume and concentration of the drip solution. It was therefore considered preferable to allow them to accumulate during each run, since the error resulting from this procedure was not very considerable[3] and appeared to have little, if any, effect on the value of the significant ratios.

Preliminary Experiments.—Four preliminary experiments were made with synthetic solutions of approximately the same total salt concentration as natural sea water, but with a considerable variation in the concentra-

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[2] The kelp used for this purpose was collected in the waters of the Penobscot Bay, Rockland, Maine, and is known scientifically as *Laminaria Saccharosa*

[3] The average total error from this source was 2.5 to 3.0% for each constituent. If this error were assumed to apply in the most unfavorable manner possible, it was not sufficient to disturb the main conclusions reached.

tion of potassium, so that the ratio of potassium to sodium ion, expressed in moles, varied from 0.0445 to 0.1052 in the various feed solutions. These solutions were analyzed only for sodium and potassium and the values of the above ratio calculated for each. The corresponding values in the drip solution varied from 0.0999 to 0.1295 and from 0.0392 to 0.0803 in the overflow. It was therefore definitely established that potassium passed through the diaphragms more readily than sodium and accumulated in the drip solution. The concentration of sodium, on the other hand, usually increased in the overflow, showing that its passage through the diaphragms was retarded.

Experiments with Natural Sea Water.—A sample of sea water was collected at Winthrop, Mass., at a point where the full sweep of the ocean was effective, so that the probability of obtaining a representative sample would be as great as possible. It was found to contain less than 3% total salts, as compared with 3.5% in the average ocean water.

Slightly more than 80 liters of sea water was used to start with, and this was run through a series of eight cells. The drip and overflow solutions were collected and measured and the drip solution used as the feed for a second run with four cells. The volumes obtained from these two runs were as follows:

		Liters		Liters		Liters
No. 1.	Seawater	80.160	Drip	36.530	Overflow	37.620
No. 2.	Feed	36.015	Drip	14.825	Overflow	17.760

Considerable evaporation took place from the drip solution at the exposed outer surface of the cells. The overflow was collected in a bottle closed by a stopper containing a small air vent. Hence the total evaporation was assumed to apply to the drip solution and the concentration of each constituent was corrected accordingly. No correction was made for the crystals which formed at the outer surface of the diaphragms. The difference between the totals in the feed solution and the corresponding sum in the overflow and drip solutions was considered a measure of its extent, since considerable care was taken to prevent accidental loss of any of the solutions. It amounted to about 3% in the first run and about 0.25% in the second. All five solutions were analyzed for Cl, Br, SO_4, Na, K, Ca and Mg. The results are recorded in Table I.

TABLE I

GRAM EQUIVALENTS PER LITER

Run	Ion	Feed soln.	Overflow soln.	Drip soln.	Drip corrected	Drip (corr.) minus feed	% Change
1	Cl	0.4348	0.4373	0.4722	0.4055	−0.0293	− 6.73
1	Br	.0022	....	.0049	.0040	+ .0018	+81.8
1	SO_4	.0430	.0436	.0494	.0424	− .0006	− 1.39
1	K	.0093	.0077	.0144	.0125	+ .0030	+32.25
1	Na	.3516	.3575	.3853	.3308	− .0208	− 5.91
1	Mg	.0848	.0848	.0940	.0807	− .0041	− 4.83
1	Ca	.0178	.0184	.0208	.0177	− .0001	− 0.56
2	Cl	.4722	.4980	.5531	.4491	− .0231	− 4.89
2	Br	.0049	....	.0069	.0056	+ .0009	+18.36
2	SO_4	.0494	.0522	.0616	.0499	+ .0005	+ 1.01
2	K	.0144	.0105	.0358	.0285	+ .0141	+97.9
2	Na	.3853	.4105	.4348	.3525	− .0328	− 8.51
2	Mg	.0940	.0836	.1056	.0857	− .0083	− 8.83
2	Ca	.0207	.0184	.0304	.0241	+ .0034	+16.42

The ratio K/Na had the values 2.64×10^{-2}, 3.73×10^{-2} and 2.15×10^{-2} in the feed, drip and overflow for Run 1, and 3.73×10^{-2}, 8.23×10^{-2} and 2.55×10^{-2} in the feed, drip and overflow for Run 2. The figures in the last column brought out the striking fact that both potassium and bromide ions showed a marked increase in the drip solution as compared with the feed, while sodium, magnesium and chloride ions showed a decided decrease. Sulfate ion was practically unchanged, while calcium ion was essentially unchanged in the first experiment, but increased sharply in the second. The value for magnesium in the overflow from Run 2 was for some reason too low, probably an analytical inaccuracy.

Experiment 1 used freshly prepared cells and required 256 hours to complete. Experiment 2 used cells already in use for one week and required 122 hours to complete. Semi-quantitative tests made daily for potassium by the cobaltinitrite method showed an essentially constant relation between the potassium concentrations of the feed, drip and overflow solutions. This indicated that the diaphragms did not lose their efficiency during the experiments and that a freshly prepared cell was no more effective than one which had been in use for ten days. Some cells were used continuously for about six weeks without losing their effectiveness.

In order to determine how far the accumulation of potassium would proceed, these solutions were subjected to further action of the alginate diaphragms in such a manner that the potassium should be accumulated as completely as possible in the drip at the end of the series of experiments and diminished as far as possible in the overflow. This was accomplished by combining drip and overflow from intermediate experiments and re-running these solutions. Fifteen separate experiments were made and the final solutions to be analyzed were collected in four portions. No. 4 was expected to be most concentrated in potassium, followed by Nos. 3, 2 and 1 in decreasing order. The volumes of these solutions were as follows: No. 1, 44.080 liters; No. 2, 7.090 liters; No. 3, 0.900 liter; No. 4, 0.610 liter. The complete record for the series gave: original sea water, 80.780 liters; solutions Nos. 1, 2, 3, 4, 52.680 liters; samples, 2.810 liters; evaporation, 24.930 liters; losses, 0.360 liter. The percentage loss was 0.44, a reasonable figure when the nature and extent of the operations was considered. The four solutions were analyzed only for sodium, potassium and sulfate. Results are recorded in Table II.

In columns 6 and 7 the concentrations of potassium and sulfate ion were corrected to the value they would have had if the sodium concentration had remained the same as that of the original sea water. In column 8 the volumes were corrected on the same basis. The sum of these corrected volumes was less than that of the sea water by 0.35 liter, while the losses as noted in a preceding paragraph were 0.36 liter. The changes in the potassium concentration (col. 9) were very striking; in solution No. 1 (overflow), the concentration had decreased by almost 11%, while in No. 4 (drip), it had increased almost 500%. Solutions 2 and 3 showed increases of about 11 and 54%, respectively, results which were entirely logical when their method of collection was considered.

The increases in the concentration of sulfate ion progressed from about 1% in No. 1 to about 30% in No. 4. Hence, there was a slight tendency for the diaphragms to

TABLE II

GRAM EQUIVALENTS PER LITER

		As determined			Corrected			% Change	
Soln.	Vol.	K	SO_4	Na	K	SO_4	Vol.	K	SO_4
S. W.	80.78	0.0093	0.0860	0.3516	0.0093	0.0860	80.78		
1	44.08	.0103	.1096	.4425	.0083	.0870	55.48	− 10.75	+ 1.16
2	7.09	.0251	.2012	.7902	.0103	.0895	15.93	+ 10.75	+ 4.07
3	0.90	.0639	.4460	1.5655	.0143	.1002	4.01	+ 53.75	+16.51
4	.61	.1681	.3456	1.0886	.0543	.1116	1.89	+483.87	+29.76
Samples	2.81	....	....	....	.0145	.1001	3.12	+ 55.91	+16.39
Sum	55.49	....	....	....	....	....	80.43	....	...

favor the passage of sulfate ions, though inconsiderable when compared to their action with reference to potassium and bromide ions. The molar ratio K/Na in solution No. 4 was 15.48 × 10^{-2} and the rate of its change, by further passage through the cells, appeared to be very slow.

Experiments with "Bittern" Solutions.—In order to discover whether there was a definite limit beyond which the above-mentioned ratio could not be increased by passage of the solution through the alginate diaphragms, experiments were made with artificial "bittern" solutions in which the ratio K/Na had a value between 0.166 and 0.178. Three such experiments were made and the resulting nine solutions were each analyzed for potassium, sodium and sulfate. Results were recorded in Table III. In Run 1, the procedure was the same as that employed with sea water. The tendency for salts to crystallize around the edges of the cells was so much greater with these concentrated solutions that the crystals were scraped down with a spatula and added to the drip solution in Run 1. In Run 2 distilled water was fed by means of wicks onto the upper, outer surfaces of the cells and greatly diminished the amount of crystallization. In Run 3, an approximately $M/100$ solution of hydrochloric acid was applied with the wicks instead of distilled water.

TABLE III

Run	Soln.	Volume	Moles per Liter K	Na	SO_4	Molar K/Na × 10^{-2}	Ratio Na + K/SO_4
1	Feed	0.985	0.3490	2.1217	0.3462	16.45	7.13
1	Overflow	.830	.3756	2.2386	.3587	16.78	7.28
1	Drip	.085	.4734	2.8800	.4935	16.43	6.79
2	Feed	2.950	.4050	2.2649	.4866	17.83	5.48
2	Overflow	2.425	.3876	2.2150	.4702	17.49	5.53
2	Drip	0.425	.4680	2.7688	.5656	16.90	5.72
3	Feed	2.325	.3876	2.2150	.4702	17.49	5.53
3	Overflow	1.770	.3791	2.1747	.4652	17.43	5.49
3	Drip	0.500	.4088	2.3698	.4851	17.25	5.72

A glance at these results showed that both the K/Na and the Na + K/SO_4 ratios remained substantially constant and therefore that the solutions had passed through the diaphragms practically unaltered in composition. The total losses due to crystallization at the surface of the cells were 0.64, 2.62 and 1.66, respectively.

Experiments with Soap.—Although more troublesome to accomplish, it was found that similar diaphragms could be prepared using a soap solution in place of the sodium alginate and precipitating with a solution containing calcium and magnesium salts. Such a cell was prepared and two runs were made with it, using the overflow solution from No. 1 as the feed solution for No. 2. Analyses were made for sodium, potassium and sulfate only. Results were shown in Table IV. The K/Na ratios were 11.24 × 10^{-2}, 12.49 × 10^{-2} and 11.80 × 10^{-2} in the feed, drip and overflow for No. 1 and 11.80 × 10^{-2}, 13.98 × 10^{-2} and 11.32 × 10^{-2} in the feed, drip and overflow for No. 2. The ratio Na + K/SO_4 remained sensibly constant. The total crystallization losses were 4.49 and 0.65%, respectively.

TABLE IV

GRAM EQUIVALENTS PER LITER

Run	Ion	Feed soln.	Overflow soln.	Drip soln.	Drip corrected	Drip minus feed	% Change
1	K	0.0455	0.0472	0.0538	0.0408	−0.0047	−10.33
1	Na	.4046	.3998	.4305	.3259	− .0787	−19.45
1	SO_4	.0472	.0468	.0514	.0389	− .0083	−17.58
2	K	.0472	.0450	.0836	.0604	+ .0132	+27.96
2	Na	.3998	.3975	.5980	.4320	+ .0322	+ 8.06
2	SO_4	.0468	.0486	.0730	.0529	+ .0061	+13.03

It was of interest to note that while Run 1 showed a rather large decrease in the concentrations of all three constituents, No. 2 compensated by showing an increase in all three. The net result was a decrease in sulfate and sodium and an increase in potassium. It was, therefore, evident that the diaphragms prepared from soap acted similarly to the alginate diaphragms so far as these three constituents were concerned, though its selectivity was less pronounced.

Experiments with Casein.—Proceeding in a similar manner, diaphragms were prepared by using the casein–sodium carbonate solution and precipitating with a solution containing calcium and magnesium salts. Two experiments were made in this series also, using the overflow from No. 1 as the feed solution for No. 2. The resulting solutions were analyzed for sodium, potassium, calcium, magnesium and sulfate. Because casein formed colloidal micelles with the calcium and magnesium, which although stable for some time gradually coagulated and separated from the solution, it was difficult to secure samples of these solutions which could be counted upon to be representative with respect to their calcium and magnesium content. The uncertainty arising from this source, however, was not very great. Table V shows the results of these experiments.

In both experiments the ratio K/Na *increased* in the overflow, and *decreased* in the drip as compared with its value in the feed solution. The values were 19.84 × 10^{-2}, 18.89 × 10^{-2} and 21.19 × 10^{-2} for feed, drip and overflow in No. 1 and 21.19 × 10^{-2}, 20.36 × 10^{-2} and 22.63 × 10^{-2} for corresponding solutions in Run 2.

No analysis was made upon the crystals which separated at the outer surfaces of the diaphragms in the experiments

TABLE V

GRAM EQUIVALENTS PER LITER

Run	Ion	Feed soln.	Overflow soln.	Drip soln.	Drip corrected	Drip minus feed	% Change
1	K	0.0864	0.0870	0.0953	0.0922	+0.0058	+ 6.71
1	Na	.4354	.4104	.5044	.4881	+ .0527	+12.10
1	Ca	.0366	.0452	.0298	.0289	− .0077	−21.03
1	Mg	.0960	.0934	.1191	.1153	+ .0193	+20.10
1	SO_4	.0620	.0620	.0716	.0693	+ .0073	+11.77
2	K	.0870	.0911	.0992	.1019	+ .0149	+17.12
2	Na	.4104	.4024	.4871	.4915	+ .0611	+19.76
2	Ca	.0452	.0280	.0304	.0312	− .0140	−30.97
2	Mg	.0934	.1256	.1072	.1102	+ .0168	+17.98
2	SO_4	.0620	.0604	.0720	.0740	+ .0120	+19.36

with any of these three diaphragm materials. The calculation of the total amounts of each ion in the three solutions from any of these experiments and the estimation of the loss by taking the difference between drip plus overflow and feed showed that these crystals were almost certainly not of one particular variety such as sodium chloride. Even assuming that they were sodium chloride only and recalculating the K/Na ratios, a substantial change in its value in the drip as compared with its value in the corresponding feed solution still remained, with all three diaphragm materials.

Theoretical Discussion

Two possible explanations of the selective action noted above have suggested themselves: (a) chemical action, (b) physico-chemical action.

(a) **Chemical Action.**—The assumption that this effect was due to chemical action of the diaphragm material would require that combination, probably salt formation, took place on one side and decomposition or dissociation on the other side of the diaphragm. This could possibly occur if the solutions in contact with the two sides of the membrane differed in their *P*H values. On the inside a thin layer might be formed which, through hydrolysis of the calcium alginate, could increase its *P*H value with respect to the remainder of the solution. On the outside since the liquid layer was a thin film, the emerging alginates might be decomposed by absorbed carbon dioxide. This seemed scarcely likely since alginic acid can be dissolved in a solution of either sodium carbonate or bicarbonate with the liberation of carbon dioxide.

(b) **Physico-chemical Action.** (1) **Ionic Radii.**—Assuming that these membranes were made up of solid particles, there would naturally exist very small pores or passages through which the solution could pass and form a continuous phase. Should the radius of any particular ion be too great to allow its passage through these pores, it would of course be excluded from the drip solution. The experimental observations do not appear to be explained by such a sieve action.

(2) **Adsorption.**—The more probable explanation appeared to be that the diaphragms adsorbed some ions or molecules of the salts dissolved in the feed solution much more strongly than others and in consequence a thin layer of solution was built up at the surface of the diaphragm in which the concentrations of the various salts, or dissociation products from them, would be considerably different from the corresponding concentrations in the main body of the solution. Accordingly, when water passed through the diaphragms and osmosis caused the dissolved salts to pass through as well, it would be logical to expect that the solution which appeared on the other side would differ from the original solution and approximate to the composition of the layer at the surface of the diaphragm. In other words, the concentrations of the particular ions or molecules which were most strongly adsorbed by the diaphragm would be increased in the drip solution at the expense of other ions or molecules present in the feed solution.

An objection to this explanation might be that, since the calcium salts of alginic acid, the fatty acids and casein acids are capable of dissociation, the adsorption occurred because of the entrance of one or more of the ions into the lattice of the solid instead of being adsorbed at the solid–liquid interface. The forces holding the adsorbed ion in that position would in consequence keep it under a very considerable restraint. If this were the case, the membranes would eventually become saturated with the adsorbable ions. It has already been pointed out that this does not appear to be the case. On this assumption also, the concentration changes would have to be explained as being due to the deficiency of the adsorbed ions or molecules in the drip solution. It has been pointed out that this explanation does not appear to be adequate.

The fact that all of the three materials used for the preparation of the diaphragms were colloidal in their behavior and properties was almost certainly significant and lends strength to the adsorption theory of the explanation of their selective action.

Although it would not be safe to make any generalizations on the basis of so limited a number of examples, it was very interesting to note that the two materials which favored potassium are organic acids composed only of carbon, hydrogen and oxygen, while casein which reversed this selectivity is amphoteric and a protein.

In conclusion, I wish to express my grateful thanks to Professor Grinnell Jones of Harvard University. As his private assistant, space and equipment were afforded me for the carrying out of this work. Also, I am indebted to him for many helpful suggestions and criticisms.

Summary

Diaphragms have been described which exhibited a selective osmotic action with respect to the various ions or molecules present in the solution.

When either *sodium alginate* or *soap* was used in constructing the diaphragm, the selective action favored potassium and retarded sodium ions, or their corresponding salt molecules. The alginate diaphragms also favored bromide at the expense of chloride ions and to a much smaller extent favored sulfate over chloride ions and calcium over magnesium and sodium ions.

When *casein* was used as the diaphragm material, the selective action was *reversed* with respect to sodium and potassium compounds, *i. e.*, sodium was favored and potassium retarded. Calcium also appeared to be greatly retarded.

All materials which were found to exhibit a selective osmotic action were *colloidal* in their behavior and properties.

It has been suggested that this phenomenon may be explained as being due to *adsorption* of the various ions or molecules at the surface of the diaphragm.

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[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF THE UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD, UNIVERSITY OF ST. ANDREWS]

The Constitution of Inulin. Synthesis of 3,4,6- and 1,4,6-Trimethyl-γ-fructose

BY T. N. MONTGOMERY

It is well known that inulin on methylation and subsequent hydrolysis yields 3,4,6-trimethylfructose, together with a small amount of tetramethyl-γ-fructose.[1] In view of the liquid nature of the products, and of the fact that no satisfactory evidence is available that the trimethyl sugar consists solely of 3,4,6-trimethylfructose, it is not only desirable to confirm by synthesis the structure of this key substance to the constitution of inulin, but of even greater importance to establish in this way the homogeneity of the trimethylfructose obtained from the polysaccharide.

In a recent communication from this Laboratory[1d] proof was given that the sirupy trimethylfructose is a single chemical individual. This rested on the fact that (a) when the sugar was treated with acetone containing hydrogen chloride and specimens of the product isolated at various stages as the reaction proceeded, and (b) when the monoacetone derivative of the sugar thereby produced was subjected to graded hydrolysis, no evidence of separation of the trimethylfructose into different fractions could be detected. Different specimens of trimethylfructose monoacetone isolated in this way, however, showed considerable variation in specific rotation, but this was attributed to α- and β-isomerism. Further work has been devoted to the subject, and it is now possible to confirm by positive results the homogeneity of the trimethyl sugar, and to establish beyond doubt the isomerism of the monoacetone derivative, by a synthesis of 3,4,6-trimethylfructose. The outline of the scheme of synthesis is as follows

Fructose ⟶ β-diacetonefructose ⟶ 1-benzoyl-β-diacetone-fructose ⟶ 1-benzoylfructose ⟶ 1-benzoyl-γ-methylfructoside ⟶ 1-benzoyl-3,4,6-trimethyl-γ-methylfructoside ⟶ 3,4,6-trimethyl-γ-methylfructoside ⟶ 3,4,6-trimethylfructose.

Despite the fact that 3,4,6-trimethylfructose is a liquid and difficult to purify, the synthetic sugar shows good agreement in properties with that derived from methylated inulin. Both yield the same crystalline phenylosazone, and the similarity in the polarimetric curves of the reaction of condensation of the sugar with acetone (A and B, Fig. 1), and of the hydrolysis of the resulting product (D, Fig. 1) leave little doubt as to the identity of the two sugars.

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[1] (a) Irvine and Steele, *J. Chem. Soc.*, 1474 (1920); (b) Haworth and Learner, *ibid.*, 619 (1928); (c) Haworth, Hirst and Percival, *ibid.*, 2384 (1932); (d) Irvine and Montgomery, THIS JOURNAL, **55**, 1988 (1933).