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A STUDY OF THE SODIUM AMALGAM ELECTRODE FOR THE DETERMINATION OF SODIUM ION

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Preparatory to an investigation of the concentration of sodium ion in various biological fluids which is now in progress in this laboratory, it was deemed necessary to investigate the reliability of the sodium amalgam electrode for determining electrometrically the concentration of this ion under such conditions as exist in these fluids.   Electrometric determinations were therefore made in aqueous solutions of various concentrations of pure sodium chloride which were not air-free, as well as of solutions of sodium chloride mixed with chlorides of other cations (such as potassium and calcium) that are present in biological fluids and with protein.

Although quite a number of electromotive studies of sodium amalgams and alloys had been made, up to 1908 only one short article by Byers[1] gave some data on determining sodium-ion concentration by a continuously dropping amalgam electrode. The ingenious methods of determining the electrode potentials of sodium and potassium employed by Lewis and Kraus[2] and Lewis and Keyes,[3] by which they were able to obtain constant values for a considerable time, served to show the possibilities of these electrodes.   Accordingly, Allmand and Pollack[4] employed a dropping sodium amalgam electrode in their study of the free energy of dilution of sodium chloride, and Donnan

[1] Byers, THIS JOURNAL, **30**, 1584 (1908).

[2] Lewis and Kraus, *ibid.*, **32**, 1457 (1910).

[3] Lewis and Keyes, *ibid.*, **34**, 119 (1912).

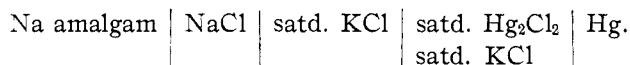[4] Allmand and Pollack, *J. Chem. Soc.*, **115,** 1021 (1919).

and Allmand[5] employed a potassium amalgam electrode to study ionic equilibrium across a semipermeable membrane.

Materials and Apparatus

The sodium amalgam was prepared by electrolyzing a saturated solution of sodium chloride using as a cathode mercury purified by Hulett's[6] method. The amalgam so obtained was filtered, diluted with additional mercury, washed and dried. This amalgam was found upon analysis to contain 0.1659% of sodium. The amalgam was analyzed by treating with 0.1 N hydrochloric acid, the excess acid being titrated with 0.02 N sodium hydroxide using methyl red as an indicator.

All the sodium chloride used in this investigation was prepared as follows. A solution of sodium hydroxide made by dissolving metallic sodium in water was neutralized by distilling over hydrochloric acid from a 31% solution. Into this solution hydrogen chloride was passed and the precipitated sodium chloride was redissolved and again treated with hydrogen chloride. The salt obtained by this second preparation was used in the experimental work. The potassium chloride used was purified by treating c. p. material with boiling distilled water. The hot solution was filtered and the potassium chloride obtained from this solution showed no sodium by the flame test. The ammonium chloride used was a pure imported material. The calcium chloride was prepared by neutralizing a pure calcium carbonate with hydrochloric acid; the zinc chloride was prepared by neutralizing a pure zinc oxide with hydrochloric acid.

The sodium amalgam electrode was like that used by Lewis and Kraus[2] except that at the bottom of the electrode vessel there was a stopcock added for draining the amalgam that had been allowed to drop off the electrode. The cell may be schematically represented

$$\text{Na amalgam} \mid \text{NaCl} \mid \text{satd. KCl} \mid \begin{array}{c} \text{satd. Hg}_2\text{Cl}_2 \\ \text{satd. KCl} \end{array} \mid \text{Hg.}$$

All the apparatus was kept in an air thermostat which was regulated to $25° \pm 0.1°$. The measurements were made with a Leeds and Northrup potentiometer using a certified Weston standard cell for reference. Readings were made to 0.0002 volts.

Experimental Results

The reliability of this electrode for determining sodium-ion concentration when only sodium salts are present in aqueous solutions, may be seen from Table I.

TABLE I

Conc. of NaCl	Voltage obs.	Voltage calc.
0.2	2.1483	. . . .
0.1	2.1650	2.1649
0.02	2.2035	2.2042
0.01	2.2198	2.2213

To determine just how fast the amalgam is impoverished with respect to sodium concentration by reacting with the solvent, readings were

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[5] Donnan and Allmand, *J. Chem. Soc.*, **105**, 1941 (1914).

[6] Hulett, *Phys. Rev.*, **33**, 307 (1911).

taken at 5-minute intervals at concentrations of sodium chloride noted in Table II.

TABLE II

Conc.	Read at start	Minutes					New surface
N		5	10	15	20	25	
0.2	2.1482	2.1482	2.1480	2.1476	2.1470	2.1460	2.1483
0.1	2.1650	2.1648	2.1647	2.1643	2.1638	2.1635	2.1652
0.02	2.2035	2.2034	2.2030	2.2020	2.2010	2.2005	2.2034
0.01	2.2198	2.2190	2.2185	2.2180	2.2170	2.2160	2.2199

In this series of experiments the electrode after being in contact for 16 hours with a 0.2 N sodium chloride solution gave a reading of 1.671 volts. Upon renewing the amalgam surface of the electrode, by permitting about 6 drops of amalgam to flow out, a reading of 2.1484 volts was obtained. In a similar experiment a 0.01 N sodium chloride solution gave a reading of 1.7087 volts after being in contact with the electrode for 18 hours; upon renewal of the surface of the electrode 2.2195 volts was read—the usual value of this concentration being 2.2198 volts.

It has been found that when an amalgam is treated with an aqueous solution of a salt of a metal that can amalgamate, a mixed amalgam is obtained. The effect of varying concentrations of potassium, ammonium, calcium and zinc chlorides on the voltage given by a 0.1 N sodium chloride solution was, therefore, studied. To determine, furthermore, the progressive replacement, readings were also taken at 5-minute intervals for 25 minutes without changing the surface of the amalgam electrode. Except for the presence of the other salt in the solution in the amalgam half-cell, no other change was made in the cell. The results given in Table III are

TABLE III

VOLTAGES GIVEN BY A 0.1 N SODIUM CHLORIDE IN THE PRESENCE OF OTHER SALTS

Admixed salt	Conc.	Initial reading	Minutes				
	N		5	10	15	20	25
KCl	0.1	2.1577	2.1560	2.1558	2.1433	....	....
	0.075	2.1589	2.1597	2.1592	2.1505	2.1327	2.1252
	0.05	2.1595	2.1608	2.1606	2.1592	2.1545	2.1425
	0.025	2.1613	2.1621	2.1615	2.1535	2.1515	2.1272
	0.01	2.1638	2.1638	2.1637	2.1615	2.1605	2.1550
NH₄Cl	0.025	2.1575	2.1385	....	....	....	....
	0.01	2.1636	2.1550	2.1425	2.1357	2.1330	....
	0.001	2.1650	2.1638	2.1638	2.1610	2.1550	....
CaCl	0.1	2.1625	2.1250	2.0082	....	....	....
	0.075	2.1639	2.1270	2.1074	2.0790	2.0647	....
	0.05	2.1657	2.1330	2.1170	2.0950	2.0480	....
	0.025	2.1648	2.1634	2.1472	2.1320	2.1245	2.1115
	0.01	2.1649	2.1642	2.1596	2.1452	2.1420	2.1328
	0.001	2.1650	2.1646	2.1643	2.1642	2.1640	2.1630
ZnCl₂	0.025	2.1635	2.1622	2.1618	2.1618	2.1614	2.1608

average values obtained in three series of readings in which the initial
readings did not differ by more than 0.4 mv. from the mean values, and
the interval readings by no more than 2 mv. from the mean, a limit that
was not considered too liberal since in each case the decomposition of
the electrode was due both to the water and the replacing cation.

Blanks in Table III signify that no steady reading could be obtained
after the interval preceding. In the case of ammonium chloride it was
found impossible to make any measurements at concentrations above
0.025 N of this salt, as the sodium amalgam was very quickly replaced
by the ammonium radical with a puffing of the amalgam surface. In
concentrations of calcium chloride over 0.025 N great trouble was experi-
enced owing to the rapid generation of hydrogen and decomposition of
the amalgam. With 0.025 N zinc chloride there was no generation of
gas at the electrode; moreover, reproducible measurements could be ob-
tained without difficulty even at the intervals.

The effect of the presence of gelatin was next studied. The gelatin
upon analysis gave 1.825% ash, chiefly calcium oxide. All the salt gelatin
solutions were found by the indicator method to be at a P_H 4.7 to 4.8.

TABLE IV

VOLTAGES OBTAINED WITH 0.1 N SODIUM CHLORIDE CONTAINING 0.025% OF GELATIN
AND ADDED SALT

Salt added	Conc. N	Initial reading	Minutes				
			5	10	15	20	25
None	....	2.1652	2.1645	2.1624	2.1610	2.1605	....
CaCl₂	0.05	2.1652	2.1550	2.1375	....	....	....
	0.025	2.1637	2.1550	2.1485	2.1460	2.1445	....
ZnCl₂	0.025	2.1675	2.1654	2.1648	2.1645	2.1642	2.1632

Except in the presence of 0.025 N zinc chloride there was a generation
of hydrogen which, owing to the viscosity of the solution, formed a foam on
the surface of the electrode and by disturbing the contact prevented steady
readings after the intervals noted in Table IV. When the 0.1 N sodium
chloride solution contained 1% and 2% of gelatin, readings could be obtained
only by letting the amalgam drop continually from the electrode during
the reading. With dog's blood serum, however, that contained about 8%
protein no trouble was experienced, the first reading being 2.1509 volts,
after 5 minutes 2.1502, 10 minutes 2.1497, and 25 minutes, 2.1485. Re-
newal of the amalgam surface gave 2.1510 volts.

Since the bridge and calomel half-cell were saturated with potassium
chloride, there was no appreciable diffusion potential at that liquid junction.
As for the liquid junction between the solutions in the amalgam half-cell
and the bridge, the diffusion potentials of potassium, ammonium and so-
dium chlorides against the saturated potassium chloride may, according

to data of Akerlof[7] be taken as 0.0000 volts while that of 0.1 N, 0.075 N, 0.15 N and 0.025 N calcium chloride are not greater than 0.002, 0.0015, 0.001 and 0.0005 volts respectively; 0.025 N zinc chloride is equal to about 0.001 volt. As these potentials oppose the e.m.f., the corresponding e.m.f.'s in Tables III and IV would be increased by quantities of these magnitudes.

Discussion

On the basis of the reading given for 0.2 N sodium chloride solution there have been calculated in Table I values for 0.1 N, 0.02 N and 0.01 N. In these calculations there was taken into account the degree of dissociation at the various concentrations. While the experimental value for 0.1 N is checked very closely, that of 0.02 N is 0.0007 volt less, and that of 0.01 N, 0.0015 volt less than the calculated value. As the solution is diluted, the amalgam is apparently more easily attacked, and even in the short time required for measurement enough sodium is lost by the amalgam to make it a weaker electrode with a lower potential. It is also very probable that the activity of the sodium ion is changed upon dilution—only 6% in a dilution from 0.2 N to 0.01 N. From Table II it may be seen that as time passes the voltage drops because of the gradual decomposition of the amalgam, and that the decomposition is greater the more dilute the solution.

In the case of 0.1 N sodium chloride solutions mixed with other salts, three considerations must be kept in mind. The common ion effect (Cl^-) will tend to decrease the Na^+ concentration; on the other hand, the presence of the second salt may activate the sodium ions, which would be equivalent to increasing the Na^+ concentration (salt effect), as had been so strikingly shown by Akerlof[7] in the case of H^+. These two results may counterbalance as had been found by Brönsted[8] who concludes that in the case of uni-univalent salts the simple gas laws are valid for ions in salt solutions. The third and most important effect is the replacement of some of the sodium in the amalgam by the cation, the electrode having a lower potential against the solution. The amount of replacement will depend principally on the chemical properties of the cation and its concentration as well as on the character of the amalgam formed by the replacing cation.

In the presence of hydroxyl ions formed by the decomposition of the amalgam, calcium ions will tend to be precipitated as calcium hydroxide upon the surface of the amalgam. It has been found by Walker and Patterson[9] and Lewis and Jackson[10] that minute particles on the surface of amalgams catalyze the decomposition of the amalgams. The deposition

[7] Akerlof, *Z. physik. Chem.*, **98**, 260 (1921).

[8] Brönsted, *Kgl. Danska Videnskab. Selskab. Math.-fys. Medd.*, **3**, No. 9 (1920).

[9] Walker and Patterson, *Trans. Am. Electrochem. Soc.*, **3**, 185 (1903).

[10] Lewis and Jackson, *Proc. Am. Acad. Arts Sci.*, **41**, 403 (1901).

of calcium hydroxide explains the copious generation of hydrogen in the case of calcium chloride solutions and might also explain why it has been found impossible, for example by Smith and Bennett,[11] to prepare by electrolysis in aqueous solution an amalgam with over 0.09% of calcium. In the case of zinc chloride, since any zinc hydroxide that might be formed on the surface would dissolve in the excess of hydroxyl ions as sodium zincate or the zincate ion, ZnO_2, no catalytic decomposition of the amalgam takes place.   The fact that in the presence of zinc chloride the gelatin solutions gave no such trouble, is interesting because of the conclusions of Isgarischew[12] from experiments on the electrolysis of zinc sulfate in the presence of gelatin that adsorption compounds are formed between the zinc ion and the gelatin and that this adsorption is greatest at 0.025% concentration of gelatin.

Summary

1. The accuracy of the sodium amalgam electrode for determining sodium-ion concentration in aqueous solution has been investigated.

2.   The effect of various concentrations of ammonium, potassium, calcium and zinc chlorides and gelatin on the potential of 0.1 N sodium chloride solution has also been studied.

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MELTING POINT, LATENT HEAT OF FUSION AND SOLUBILITY

BY F. SPENCER MORTIMER

Introduction

Commercial laboratories as well as educational laboratories which are working with organic compounds are constantly confronted with questions having to do with solubility and choice of solvent for use in purifications. In the great majority of cases the desired information is not available from the published data.   In such cases it is necessary either to determine the solubility experimentally or to resort to some method of calculation. The more successful of the various methods used for calculating solubility generally employ an equation involving Raoult's freezing-point law together with the second law of thermodynamics.   Perhaps the simplest and most useful of these expressions is

$$\log N = \frac{-L}{4.58\ T} + I \tag{1}$$

[11] Smith and Bennett, THIS JOURNAL, **32**, 622 (1910).

[12] Isgarischew, *Kolloidchem. Beihefte*, **14**, 25 (1921).