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Some investigations into the Sensitivity of the Membrane Salinometer for Various Ions

By Joris M. T. M. Gieskes[1])

Summary: The sensitivity of the membrane salinometer to the various ionic species that constitute the dissolved salts in sea water is investigated. Mixtures of various salts with sodium chloride are investigated with regards to changes in the electromotive force upon dilution with water, and also with regards to changes in the composition of the mixed electrolyte. The results are expressed in terms of changes in the activity of sodium chloride. Also sea water is investigated upon a similar basis.

Einige Untersuchungen über die Empfindlichkeit des Membransalinometers für verschiedene Ionensorten (Zusammenfassung): Die Empfindlichkeit des Membransalinometers für die verschiedenen Ionensorten, welche im Meersalz vorhanden sind, wird untersucht. Mischlösungen von verschiedenen Salzen mit Natriumchlorid werden im Zusammenhang mit Veränderungen in der elektromotorischen Kraft sowohl bei Verdünnung mit Wasser, als auch bei Änderung der Zusammensetzung, untersucht. Mit der Aktivität von Natriumchlorid als Referenz werden die Resultate von modifizierten Nernst-Gleichungen beschrieben.

Koske (1964), and Mangelsdorf (1965) discuss the use of ion exchange membranes in the determination of salinity in sea water. The cell arrangement, as discussed by these authors, has proven to be vary versatile as demonstrated by Sanders, Mangelsdorf, and Hampson (1965). These authors used a membrane sensor, which could detect changes in salinity *in situ* in both open sea water and the interstitial water in the underlying sediments in an estuary. The method has also been used succesfully by Koske (1965, 1968), and by Gieskes (1967).

Koske (1964) discusses the principle upon which this salinometer is based. This author discusses the electrochemical cell

(1)   Ag/AgCl Reference sea/M+/sea water/M—/Reference sea AgCl/Ag
            water S_1 S_2 water S_1
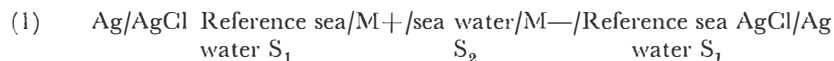
where S_1 = salinity of reference sea water, S_2 = salinity of unknown value, M+ and M— are the anion and cation membranes respectively. The electromotive force (EMF) of this cell will be dependent on the various ionic species which are present in sea water. Mangelsdorf (1966) makes use of this property of cell (1) in his detector for his method of differential chromatography of sea water.

The present investigation was made to study the effect of the various major ions in sea water on the electromotive force of cell (1). For this reason mixtures of sodium chloride with the chloride salts of potassium, magnesium and calcium, and the sodium salts of sulfate and bicarbonate were made. Dilutions were made of these mixtures with both distilled water and sodium chloride solutions. The latter investigations were made in order to gain an understanding of the changes in EMF which are related to a change in composition of the salt solution.

Theoretical Considerations

HELFFERICH (1962) discusses the membrane potential which will develop across a cell of the multi-ionic type

$$(2) \qquad AY, BY, --- / \text{ membrane } / LY, MY, ---$$

where the membrane is not permeable for ions of the type Y. In such a cell the counter ion fluxes can be considerable, and are even able to change the composition on either side of the membrane. When, however, the composition on both sides of the membrane is equal, a quasi-stationary state will be attained and no significant changes in composition will occur.

In the case of a multi-ionic cell as represented by

$$(3) \qquad AY / \text{ membrane } / AY, BY, CY, ---$$

where the membrane is not permeable to ions of the type Y, and is ideally permselective to the ionic species A only, the membrane potential will be described by the expression

$$(4) \qquad E_m = \frac{RT}{z_A F} \ln \frac{a'_A}{a''_A}$$

where a_A is the single ion activity of ion A, and z_A is the charge of the ion A. Expression (4) has also as a prerequisite that the membrane potential is dependent on the diffusion potential through the membrane only. Thus, on both sides the absence of films at the surface of the membrane is assumed. In the case where the ion exchange membrane is not ideally permselective to ions A, but also shows selectivity to other ions of like charge, the potential can be described by

$$(5) \qquad E_m = \frac{RT}{z_i F} \ln \frac{a'_A}{a''_A + \dfrac{D_B}{D_A} \cdot \dfrac{\bar{f}_A}{\bar{f}_B} a''_B + ---}$$

where D_i is the diffusion coefficient in the membrane and $\bar{f}_i$ is the activity coefficient in the membrane. For equation (5) to be valid the charges of ionic species should be equal and of the same sign. In the case where the ions have different valencies, the expression (5) will be far more complicated.

The membrane potential cannot be measured as such, but reference electrodes which are reversible to one of the ionic species, which is present on both sides of the membrane, should be used.

In the case of sea water and similar solutions silver-silver chloride electrodes will be most suitable.

We shall now consider the following electrochemical cell

$$(6) \qquad \underset{a'}{Ag / AgCl \ NaCl} / \text{ membrane } / \underset{a''}{NaCl \ AgCl / Ag}$$
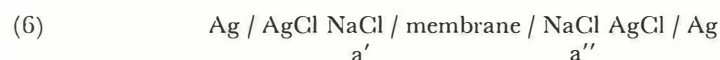
where the membrane is ideally permselective to the ions Na^+. The electromotive force will be then

$$(7) \qquad E = E_m + E_{El} = \frac{RT}{F} \ln \frac{a'_{Na}}{a''_{Na}} + \frac{RT}{F} \ln \frac{a'_{Cl}}{a''_{Cl}} = \frac{2RT}{F} \ln \frac{a'_{\pm}}{a''_{\pm}}$$

where E_m = membrane potential, E_{EL} = potential across the reference electrodes, and $a_{\pm}$ = the mean ionic activity of sodium chloride. From equation (7) it follows that (assuming $\gamma_{Na} = \gamma_{Cl} = \gamma_{\pm}$, where γ is the activity coefficient) the EMF of the cell will

be twice the membrane potential. In the case where the ion exchange membrane of the cell (6) would be ideally permselective to chloride ions the potential of the cell would be equal to zero.

In the membrane salinometer both cation and anion exchange membranes are used. Also, silver-silver chloride electrodes are used as reference electrodes. In this case, only sodium chloride is in the compartments. We can describe the cell as follows

(8)
$$\text{Ag / AgCl NaCl / M+ / NaCl / M— / NaCl AgCl/Ag}$$
$$ a' a'' a'$$
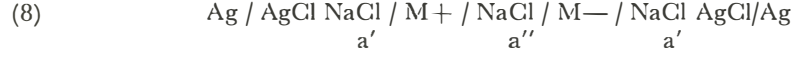
where a is the activity of the sodium chloride. In terms of single electrode potentials we then can write for the electromotive force of this cell under ideal conditions

(9)
$$E = E_{EL} + E_{in}$$

$$= \left(\frac{RT}{F} \ln \frac{a'_{Cl}}{a'_{Cl}} \right) + \left(\frac{RT}{F} \ln \frac{a'_{Na}}{a''_{Na}} - \frac{RT}{F} \ln \frac{a''_{Cl}}{a'_{Cl}} \right)$$

$$= 0 + \frac{RT}{F} \ln \frac{a'_{Na} \, a'_{Cl}}{a''_{Na} \, a''_{Cl}} = \frac{2 \, RT}{F} \ln \frac{a'_{\pm}}{a''_{\pm}}$$

where $a_{\pm}$ is the mean ionic activity of sodium chloride in solution.

From equation (9) it follows that the EMF of this system is dependent on both the activity of the cations and of the anions in solution. Usually the solution of the reference compartment is kept constant, and the solution in the central compartment is changed in concentration. In that case the changes in the EMF are due to the changes in the activities in the central compartment. The change in EMF can be described by the equation

(10)
$$\Delta E = \frac{2 \, RT}{F} \Delta \ln a_{\pm} \text{ (NaCl)}$$

In general, however, neither cation exchange membranes nor anion exchange membranes are completely permselective. Small amounts of co-ions will also be transported across the membranes. Equation (10), therefore, will show the maximum change in EMF upon dilution. HILLS (1961) discusses the case of potentials of this type, where only one electrolyte and one membrane are involved. In the case of mixed electrolyte solutions the treatment becomes very complicated if not impossible.

HELFFERICH (1962) discusses the cell of type (8) with regards to its use in electrodialysis. The current efficiency can then be conveniently described in terms of transference numbers through both the cation and the anion exchange membranes.

In our problem, however, we are faced with complicated multi-ionic mixtures, and therefore it is proposed to introduce the following equation to describe changes in the EMF of cell (8) upon dilution of the solution in the central compartment

(11)
$$\Delta E = A \frac{2 \, RT}{F} \Delta \ln a_{\pm} \text{ (NaCl)}$$

The delta symbol indicates that our interest is mainly the change in EMF upon dilution of the central solution.

The factor A describes the non-ideal behaviour of the cell assembly, due to the transport of co-ions and also due to the absence of absolute membrane diffusion control on the side of the membranes where contact is made with the reference electrolyte. The solution, which is under investigation, however, is well stirred, so that here no film develops on the membrane.

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Experimental

All measurements were carried out at temperatures of $21°$ C $\pm$ 0.5. The solution in the central compartment was well stirred with a mechanical stirrer. All dilutions were made by weight, so that all results are based on the molality scale. The temperature fluctuation can at most cause an error of 0.2% (or at 80 mV, an error of 0.16 millivolts). This error is estimated to be within the overall experimental error of the measurements. All activity coefficients were obtained from ROBINSON and STOKES (1959) at 25° C. The change of activity coefficients between temperatures of 25° and 20° C is very small, and we therefore have applied the well defined coefficients at 25° C.

All measurements were made with the American Machine and Foundry Company A-104 B and C-103 C membranes.

Results and Discussion

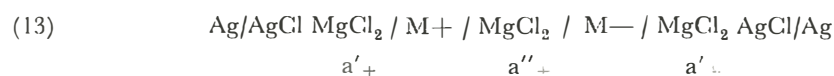### Sodium chloride solutions

KOSKE (1964) reported on dilutions of this system. Determinations were repeated with the cell of type (8), with solutions of 0.1 m and 0.7 m sodium chloride used as references. From the experimental determinations the following equation was found to be representative of the change in EMF at dilution

$$(12) \qquad \Delta E = 0{,}94 \; \frac{2 \, R \, T}{F} \; \Delta \ln a_{\pm} \; (NaCl)$$

The inaccuracy in the factor is about $\pm$ 0.005. This factor can be considered as the factor due to the non-ideal behavior of the electrode system.

Magnesium chloride solutions

In order to investigate the sensitivity of the electrode system to magnesium ions the following cell was studied

$$(13) \qquad Ag/AgCl \; MgCl_2 \; / \; M+ \; / \; MgCl_2 \; / \; M- \; / \; MgCl_2 \; AgCl/Ag$$

$$a'_{\pm} \qquad\qquad a''_{+} \qquad\qquad a'_{-}$$

In this case the ideal behavior of the membrane electrodes would lead to a change in EMF upon dilution of

$$(14) \qquad \Delta E = \frac{3}{2} \; \frac{R\,T}{F} \; \Delta \ln a_{\pm} \; (MgCl_2)$$

In this study 1.02 m and 0.115 m $MgCl_2$ solutions were used. In the first series of investigations the reference cells were filled with 1.02 m $MgCl_2$, as well as the central compartment. The average results of the two dilutions runs are presented in Figure 1 (Plate 1). The results are accurate to $\pm$ 0.2 millivolts. It can be seen that no linear relation exists between ΔE and log $a_{\pm}$ $(MgCl_2)$. This is due to the non-ideal behavior of the electrode system. At lower concentrations the dependence becomes linear with a slope of 69 millivolts. Also, dilutions were made of the 0.115 m $MgCl_2$ in the reference compartments. In Figure 2 (Plate 1) the results are plotted as a function of the mean molality, because activities could not be calculated due to the lack of data. In this case the slope is 71 millivolts, so that it is reasonable to estimate that the change in EMF upon dilution can be described by the equation

$$(15) \qquad \Delta E = 0{.}80 \; \frac{3}{2} \; \frac{R\,T}{F} \; \Delta \ln a_{\pm} \; (MgCl_2)$$

where the factor has an uncertainty of $\pm$ 0.01.

Sodium chloride and magnesium chloride solution

In sea water of a chlorinity of $19^o/_{oo}$ the concentration of sodium ions is about 0.470 Molar and of Magnesium ions the concentration is about 0.0536 Molar, with a Mg/Na ratio of 0.114. We therefore made up two solutions of the following composition:

      (a)   0.467 m NaCl and 0.259 m $MgCl_2$

      (b)   0.510 m NaCl and 0.064 m $MgCl_2$

where the concentrations are expressed in terms of molality. The second solution has a Mg/Na ratio of 0.125, which is close to that of sea water.

In the first series of dilutions the solution (a) was diluted with distilled water. Solution (a) was also present in the reference compartments. Naturally, both sodium and magnesium ions will participate in the formation of the membrane potential of the cation exchange membrane. Due to the non-ideal behavior of the membrane system, it will become virtually impossible to express the change in EMF in terms of the activities of both ionic species. We, therefore, made calculations on the basis that only sodium chloride is responsible for the change in EMF. The mean ionic activity of NaCl was calculated from the individual molalities of the sodium and chloride ions, in connection with the mean ionic activity coefficient of sodium chloride at the ionic strength of the solution. The resulting curve is represented by Curve A in Figure 3 (Plate 1). Similarly, a curve can be calculated for the case that only Mg^{++} and Cl^- ions are responsible for the change in EMF. The result is Curve B in Figure 3. It should be noted that in both calculations the factors used in equation (12) and (15) are incorporated in the results. Curve C in Figure 3 represents the results obtained from our measurements. This curve can be described by the equation

$$(16) \qquad \Delta E = 0.725 \; \frac{2\,R\,T}{F} \; \Delta \ln a_{\pm} \, (NaCl).$$

In the latter equation is assumed that the factor will take care of the deviation from ideal behavior with respect to NaCl, due to the non-ideality of the membrane and to the presence of Mg^{++} ions in solution. This procedure is, of course, not thermodynamically sound, but due to the complexity of the cell, the presence of a mixed electrolyte solution, and the non-ideal behavior, a description by means of an adequate theoretically based equation becomes impossible. In this study the main interest is the magnitude of changes in the slope with respect to ideal behavior of the cell assembly to sodium chloride. This compound is the major constituent of sea water. We contend that in such a case the factor in equation (16) does serve as a useful indication of non-ideal behavior.
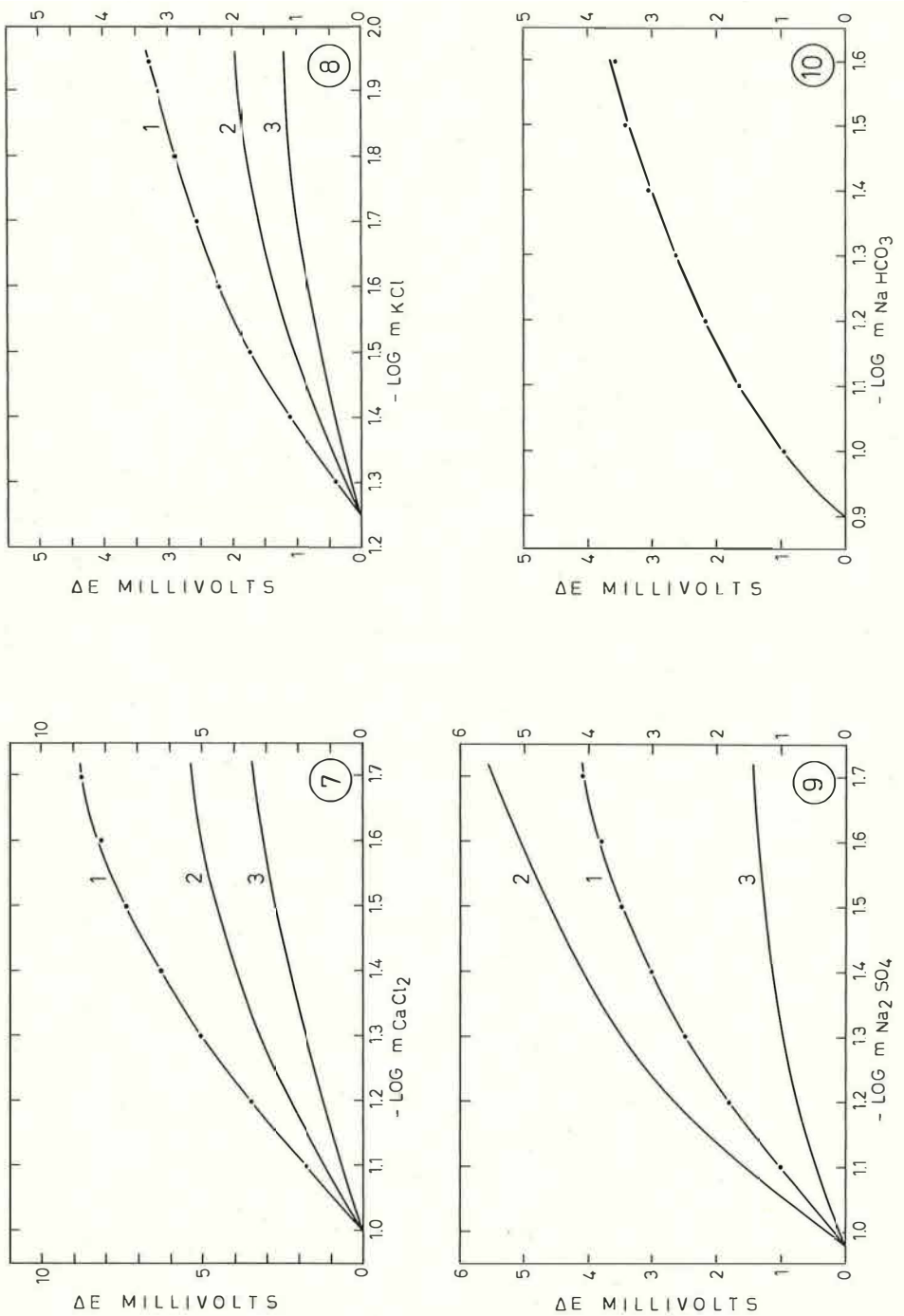
In the second series of measurements the dilutions were made initially with solution (b) in all compartments. Again calculations were carried out based on the sensitivity to Na^+ and Cl^- ions, and to Mg^{++} and Cl^- ions. Curve A in Figure 4 (Plate 1) represents the first case and Curve B the case for $MgCl_2$. Curve C again is the experimental curve. The results can be described by the equation
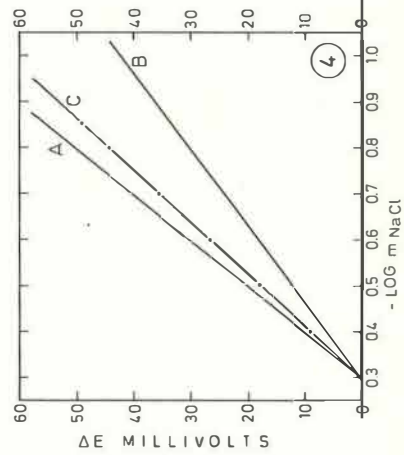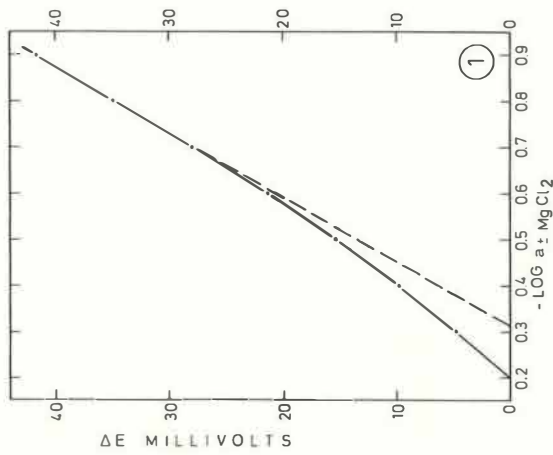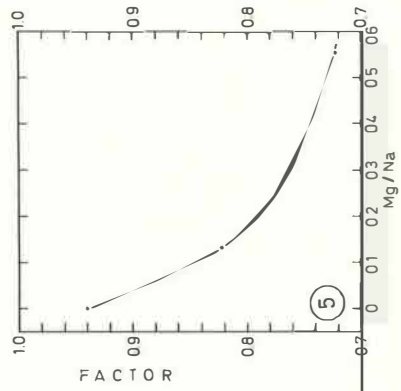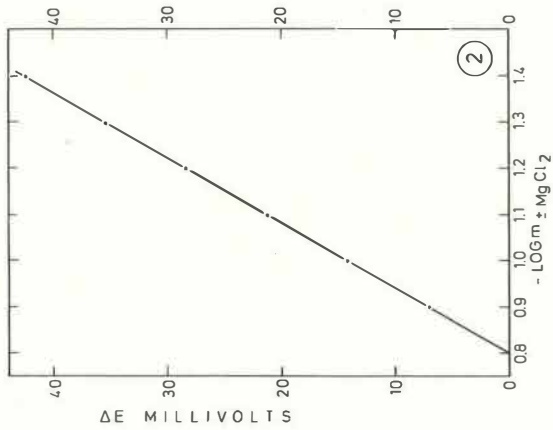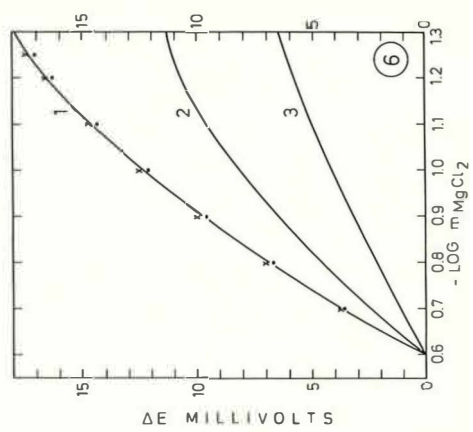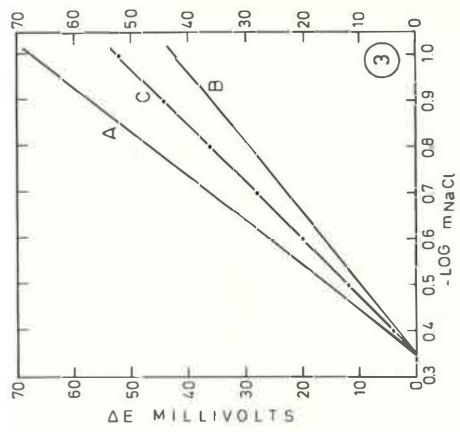
Tafel 1 (zu J. M. T. M. Gieskes)

Tafel 2 (zu J. M. T. M. Gieskes)

(17) $\Delta E = 0.823 \dfrac{2\,R\,T}{F}\, \Delta \ln a_{\pm}\ (NaCl)$

In Figure 5 (Plate 1) the factor of equations (16) and (17) is plotted as a function of the Mg/Na ratio. At a ratio of 0.114, i. e., the ratio of sea water, the factor would be equal to 0.834.

In two other sets of experiments dilutions were made of solution (a) with a 0.467 molal solution of sodium chloride. In the first series the reference cells were filled with solution (a), and in the second series they were filled with solution (b). In these experiments the sodium chloride concentration remained constant, and only the magnesium chloride concentration changed. Of course, the mean ionic activity of sodium chloride, i. e., $\gamma_{\pm}\ (m_{Na} + \times m_{Cl^-})^{1/2}$ did change in these experiments, due both to changes in the chloride concentration, and to changes in the ionic strength. In Figure 6 (Plate 1) the experimental results are represented by Curve 1. Curve 2 was calculated on the basis of sensitivity to Na^+ and Cl^- ions only, using equation (12). Curve 3 then represents the difference between the data which constitute the curves 1 and 2. This curve might be regarded as the change in EMF which is due to changes in the Mg/Na ratio. The slope of Curve 3 at a concentration of $MgCl_2$ so that $\log m MgCl_2 = -1.273$, is equal to $\Delta E / \Delta \log_m = 6.4$ millivolts. At this concentration the ratio of Mg/Na = 0.114. This slope implies that a 10% change in composition would cause a change in EMF of 0.64 millivolts.

Sodium chloride and calcium chloride solutions

In sea water the ratio of Ca/Na is equal to 0.0218. For this reason two solutions were made of the following composition

(a)   0.492 m NaCl and 0.101 m $CaCl_2$

(b)   0.487 m NaCl and 0.010 m $CaCl_2$

The latter solution has again a Ca/Na ratio similar to that of sea water.

Dilution of solution (a) gave rather inconclusive results, but a factor of 0.73 ± 0.01 in an expression of the type of equation (17) seems to describe the results quite satisfactory. The dilution of solution (b) yielded a factor of 0.93, only slightly lower than the factor for pure sodium chloride solutions. Again, dilutions were made of solution (a) with a 0.492 m NaCl solution. The results are summarized in Figure 7 (Plate 2). The relative errors of the measurements with this mixture were rather large. The results as given in Curve 3 of Figure 7 should, therefore, be regarded as showing the tendency of the change in EMF due to Ca^{++} ions upon a change in composition.

Sodium chloride and potassium chloride solutions

The ratio of potassium to sodium in sea water is about 0.0212. This suggested the following composition of the mixed electrolyte solutions.

(a)   0.505 m NaCl and 0.06 m KCl

(b)   0.505 m NaCl and 0.01 m KCl

The latter solutions has a K/Na ratio of 0.0198, which is similar to that in sea water.

Legende zu den nebenstehenden Abbildungen (Tafel 2)

Abb. 27: Changes in EMF upon dilution of 0.492 m NaCl, 0.101 m $CaCl_2$ with 0.492 m NaCl
Abb. 8: Changes in EMF upon dilution of 0.505 m NaCl, 0.060 m KCl with 0 500 m NaCl
Abb. 9: Changes in EMF upon dilution of 0.500 m NaCl, 0.104 m Na_2SO_2 with 0.500 m NaCl
Abb. 10: Changes in EMF upon dilution of 0.498 m NaCl, 0.140 m $NaHCO_3$ with 0.498 m NaCl

In this type of mixed electrolyte we have two monovalent cations. In general, however, the membrane will show specificity for one of these species. Solution (a) was diluted with water, and the results can be described by the equation

$$(18) \qquad \Delta E = 0.945 \; \frac{2\,RT}{F} \; \Delta \ln a_{\pm} \; (NaCl) \; .$$

Calculations were carried out using the molalities of sodium and chloride ions only. The factor is the same as for pure sodium chloride, indicating that no great influence on the EMF results due to the presence of small amounts of potassium.

Also dilutions were carried out on solution (b) using 0.500 m sodium chloride. Either pure 0.5 m NaCl or solution (b) was in the reference compartment. The results were very reproducible and are shown in Figure 8 (Plate 2). The "theoretical" curve was again calculated on the basis of changes in the activity of NaCl only. Curve 3 of Figure 8 represents the difference, and can again be attributed to the change in composition.

At this point it is interesting to note that MANGELSDORF (1966) found a change of 22 microvolts for a 10% change in the ratio of potassium and sodium. If this could be directly transferred to the case of pure NaCl and KCl mixtures, we estimate that Curve 3 of Figure 8 would show a slope of $\Delta E/\Delta \log m = 0.22$ millivolts at a concentration of $\log m_{KCl} = -1.97$. The latter concentration corresponds to the K/Na ratio which is equal to that of sea water. It is not possible to confirm this estimate from our data. We can, however, state that the slope at this concentration will be less than 0.50 millivolts, so that the slope seems to be of the same order of magnitude as that of Mangelsdorf.

Sodium chloride and sodium sulphate solutions

Because the membrane salinometer also makes use of an anion exchange membrane, and this membrane is not ideally permselective to chloride ions, the influence of sulphate ions might be of interest. Use was made of the following solutions.

(a)   0.500 m NaCl and 0.104 m Na_2SO_4
(b)   0.492 m NaCl and 0.028 m Na_2SO_4

The latter was again similar to sea water in composition, ı. e., as far as the SO_4/Cl ratio is concerned.

Dilutions of solution (a) were made with distilled water.

The results can be represented by the equation

$$(19) \qquad \Delta E = 0.806 \; \frac{2\,RT}{F} \; \Delta \ln a_{\pm} \; (NaCl)$$

Of course, at lower ratios that factor would increase. Therefore, sulphate ions have only minor effects on the slope.

Again dilutions were made of solution (a) with a 0.500 m NaCl solution. The results are presented in Figure 9 (Plate 2). Curve 1 represents the experimental results, Curve 2, the results based on the change of (NaCl) calculated from equation (12), and again Curve 3 tends to show the influence of the sulphate ions on the EMF of the cell if small changes in the SO_4/Cl ratio occur. The changes are again only small in magnitude.

Sodium chloride and sodium bicarbonate solutions

Even though bicarbonate only occurs in concentrations of about 0.0025 equivalents per liter, it was decided to include sodium bicarbonate in this study. The following solutions were studied

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<div align="center">

(a)   0.498 m NaCl and 0.140 m NaHCO$_3$

(b)   0.500 m NaCl and 0.055 m NaHCO$_3$

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Dilutions were made of solution (a) with distilled water. The results can be represented by the equation

$$(20) \qquad \Delta E = 0.894 \; \frac{2\,RT}{F} \; \Delta \ln a_{\pm} \, (NaCl)$$

Consequently, at sea water concentrations of bicarbonate one cannot expect much influence on the EMF.

Also dilutions were made of solution (a) with a 0.498 m sodium chloride solution, with both solution (b) and sea water in the reference compartments. The results are presented in Figure 10. The "theoretical" changes, based on equation (12), are identical to the measured values.

Sea water dilutions

Finally sea water of a chlorinity of $19^0/_{00}$ was used in all compartments and dilutions were carried out with distilled water. These results corroborated the results as obtained by KOSKE (1964). The slope of the curve of the change in EMF as a function of the logarithm of the salinity is $\Delta E / \Delta \log S = 85.4$ millivolts. From the data as reported by SVERDRUP ET AL (1942) the sodium concentration was calculated for water of a chlorinity of $19.373^0/_{00}$ and of $8.000 \; ^0/_{00}$. Then, the activities of NaCl, taken into account the molalities of sodium and chloride ions, were calculated. The mean ionic activity coefficient was used which corresponds to that of a NaCl solution of the same ionic strength. Using these data, it is found that the results can be very well represented by the equation

$$(21) \qquad \Delta E = 0.780 \; \frac{2\,RT}{F} \; \Delta \ln a_{\pm} \, (NaCl)$$

The factor of this equation is smaller than any of the factors of the simple mixed electrolyte solutions. This seems quite reasonable for the following reasons. As can be seen from the studies on the cations the calculated curves for the dilutions with sodium chloride, i. e., Curve 1 in Figure 6, 7 and 8, show lower values than the measured EMF's. From the Figures 9 and 10 it follows that for the anions the reverse is true. In the first case, the main influence was on the cation membrane potential, whereas in the second the anion exchange membrane potential was influenced by the "strange" ions. In a sea water like mixture, both anion and cation exchange membranes are affected by the presence of cations and anions different from sodium and chloride ions. These effects will presumably superimpose onto each other so that the factor for sea water ought to be lower than the lowest factor obtained in this study, i. e., 0.834 for Mg^{++} ions. The nature of the factor does not allow a prediction of its value from the measurements on the individual systems.

In general it can be concluded that the deviations from the changes in EMF upon dilution of sea water as represented by equation (21) are negligible within the normal variations in composition of sea water, and are well within the accuracy of the method, which under normal operating conditions is estimated to be $\pm \; 0.01^0/_{00}$ at best. In interstitial water, however, variations in the composition could conceivably be much higher, A study of recent sediments by SIEVER ET AL (1965) suggests that in recent sediments. i. e., the first few meters of sediment, no large variations in composition occur.

Nevertheless, we think that an accuracy of $\pm \; 0.03^0/_{00}$ in salinity is possible for these types of sediment. In actual salinity measurements use is made of standardizing solutions.

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If for interstitial water a titration is made for the determination of chlorinity, and the salinity is calculated from Cox's (1967) equation

$$S \ ^o/_{oo} = 1.80655 \ Cl \ ^o/_{oo}$$

the difference between the two salinities will be a measure of both the accuracy of the method, and of possible changes in the composition. If the latter changes are apparent, MANGELSDORF's (1965) method of differential chromatography will be the ideal method for further analysis of the changes in composition.

References

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