

## LITERATURE CITED

- Beutenmuller, William. 1901. Monograph of the Sesiidae of America north of Mexico. Mem. Amer. Mus. Nat. Hist., 1: 298-299.
- Englehardt, G. P. 1932. Bus. Proc. of the Eastern Branch of the Am. Assoc. of Econ. Entomologists. Jour. Econ. Entom., 25: 293-294.
- . 1946. North American Aegeriidae. U.S. Nat. Mus. Bul., 190: 1-222.
- Herrick, G. W. 1904. The pecan tree borer. Miss. Ag. Exp. Sta. Bul., 86: 11-15.
- Metcalf, C. L., W. P. Flint, and R. L. Metcalf. 1962. Destructive and Useful Insects, Their Habits and Control, (Ed. IV). McGraw-Hill Book Co., Inc., New York. p. 256-257.
- Peterson, Alvah. 1948. Larvae of Insects, art I. Edwards Bros., Inc., New York. p. 128-129.
- Underhill, G. W. 1935. The pecan tree borer in dogwood. Jour. Econ. Entom., 28: 393-396.
- Wallace, Philip P. 1944. Biology and control of the dogwood borer, *Synathedon scitula*, Harris. Conn. Ag. Exp. Sta. Bul., 488: 373-395.

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## CORRELATION OF SEA SALT CONCENTRATION WITH THE EMF RESPONSE OF A CATION-SENSITIVE GLASS ELECTRODE<sup>1</sup>

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### ABSTRACT

A cationic glass electrode has been used to monitor the total concentration of sea salts in both natural and synthetic sea salt solutions from 0.01 to 5.0 times natural and to 2.0 times "standard" synthetic sea water. The results have been interpreted in terms of sodium chloride activity coefficients which deviate less from unity than those in pure sodium chloride solutions.

### INTRODUCTION

Some processes for desalting sea water concentrate the sea salts without changing their relative concentration (e.g., freezing or distillation) while removing essentially pure H<sub>2</sub>O. Other procedures (e.g., hyperfiltration methods) effectively concentrate the salts together in one stream while diluting them in the other. For such processes an analytical tool for measuring "on line" total salt concentration may be useful.

Glass electrodes responding to the alkali ions Na<sup>+</sup> and K<sup>+</sup> and to the alkaline earth ion Ca<sup>++</sup> have been commercially available for some time. The activity coefficient of KCl has recently been measured as a function of concentration (0.01 to 2.5 *m*) and temperature (10° to 55° C) (1, 2) and that of NaCl has been measured as a function of concentration (to 6 *m*) and medium (3, 4, 5) by the use of such electrodes. Since sea water is a somewhat adulterated NaCl solution and since some cationic glass electrodes are highly sensitive to sodium ion concentration, a study of cationic glass electrode response to total sea salt concentration (using both natural and synthetic sea salt solutions) was carried out at 25° C.

### EXPERIMENTAL

Natural sea water was obtained from the Atlantic Ocean at Daytona Beach, Florida. It was concentrated by evaporation up to a maximum of about five times natural concentration. Eight new concentrations 0.01,

0.03, 0.1, 0.3, 2.0, 3.0, 4.0, and 5.0 times the concentration of natural sea water were prepared by dilution with water. The small amount of precipitate which came out of solution during the concentration step was removed and not taken into account. Each of the new solutions as well as the natural sea water was analyzed for chloride gravimetrically by AgCl precipitation. It was assumed that the relative concentrations of ions were the same as those given by Spiegler (6) for "standard" sea water but that the total concentration of sea salts near shore may have been increased by evaporation. By means of this assumption and the chloride analyses, the ionic strength and the sodium and chloride molalities of the solutions were calculated.

The synthetic sea water was a mixture of NaCl, KCl, MgCl<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub>. Three solutions were prepared on a weight basis: one containing 5.022 *m* NaCl and 0.1208 *m* KCl, a second containing 0.7152 *m* Na<sub>2</sub>SO<sub>4</sub> and a third containing 1.606 *m* MgCl<sub>2</sub>. These solutions were mixed with water on a weight basis to give a concentration five times that of our "standard" synthetic sea water, the latter containing

0.4756 *m* Na<sup>+</sup>  
0.0101 *m* K<sup>+</sup>  
0.0645 *m* Mg<sup>++</sup>  
0.5577 *m* Cl<sup>-</sup>  
0.02856 *m* SO<sub>4</sub><sup>--</sup>

The solution containing five times "standard" concentration was diluted to approximately 2.0, 1.0, 0.3, 0.1, 0.03, and 0.01 times "standard" on an accurate weight basis, so that concentrations were known relatively precisely.

The glass electrodes used were Beckman cationic 39137 electrodes, while the reference electrodes were Ag, AgCl electrodes of the thermal type. The reference electrodes were shorted together and allowed to equilibrate in sea salt solutions prior to use. The solutions used for the emf measurements were maintained at

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saturation with respect to AgCl by adding additional solid AgCl.

A vibrating reed electrometer, in conjunction with a Rubicon K-2 potentiometer and a Brown recorder, was used for measurement of the emf of the cell. The emf cell was immersed in a constant temperature bath controlled at 25° C to within a few hundredths of a degree. The entire bath and electrode assembly were surrounded by an aluminum shield to minimize external effects on the emf readings. The precision of individual measurements was of the order of a few hundredths of a millivolt, but reproducibility between experiments was sometimes no better than a millivolt. Reproducibility was generally poorer for relative concentrations above 1.0 times natural or "standard" synthetic sea water. Equilibrium was attained within a few hours; in some cases within 15 minutes.

Since the "standard potential" of a glass electrode has no readily interpretable meaning and changes with time, values of  $\Delta E = E_1 - E$  were recorded, where  $E_1$  and  $E$  were measured on the same day. Here  $E_1$  is the emf measured with the natural sea water or the approximately 1.0 times "standard" artificial sea water, and  $E$  is the emf measured in any other concentration. Usually two different values of  $\Delta E$  (for the same concentration) were within 0.5 mv, but sometimes deviations of more than a millivolt were observed. Two runs were made at each concentration, each run involving three different glass electrodes measured separately against the Ag-AgCl electrode.

#### RESULTS AND DISCUSSION

In each run at each concentration the three different  $\Delta E$  values were averaged. The two different average  $\Delta E$  values at each concentration were then averaged with equal weights if both runs appeared to be equally precise; if not, a higher weight was given to the average value of the run of higher precision. The results are given in Table I, while Fig. 1 shows a plot of  $\Delta E$  for natural sea salt solutions against the logarithm of the ionic strength. The data fall nearly on a straight line ( $\Delta E = 0.0155 + 0.1126 \log I$ ) and are reproducible; the data for synthetic sea salt solutions also fall very near this same line. Hence we conclude that a cationic glass electrode can be used to monitor the total concentration of sea salts in a desalination process. In such a process, however, it would probably be necessary to keep the reference electrode in its own separate compartment and have it bridged into the salt solution containing the glass electrode by means of a fritted KCl bridge.

An attempt has been made to interpret the deviations of the  $\Delta E$  vs  $\log I$  plot from a straight line in terms of changes in activity coefficients. The electrode used is not sensitive to divalent cations, but is sensitive to monovalent ions including  $H^+$ . An equation of the Nernst type, which has been used for such glass electrodes (7, 8), is given as Equation (1).

$$\Delta E = E_1 - E = \frac{RT}{F} \ln \frac{[a_{Na} + k_K a_K + k_{Ag} a_{Ag} + k_H a_H]_{ac1}_1}{[a_{Na} + k_K a_K + k_{Ag} a_{Ag} + k_H a_H]_{ac1}_1} \quad (1)$$

TABLE I  
AVERAGE  $\Delta E$  VALUES IN VOLTS vs CONCENTRATION OF SEA SALT SOLUTIONS

Approx. rel. conc.	$(E_1 - E)$	$I$	$m_{Na+}$	$m_{Cl-}$
Natural Sea Salt Solutions				
0.01	-0.2250	0.007253	0.004873	0.005680
.03	- .1716	.02188	.01470	.01713
.1	- .1130	.07303	.04906	.05719
.3	- .0607	.2195	.1475	.1719
1.0*	0	.7494	.5034	.5868
2.0	+ .0353	1.477	.9923	1.157
3.0	+ .0555	2.285	1.535	1.789
5.0	+ .0883	3.904	2.623	3.057
* "Standard" sea water (6) shows $m_{Na+} = 0.4756$ , $m_{Cl-} = 0.5544$ and $I = 0.7078$ .				
Synthetic Sea Salt Solutions				
0.01	-0.2190	0.007753	0.005172	0.006100
.03	-0.1730	.02123	.01416	.01670
.1	-0.1118	.07190	.04796	.05658
.3	-0.0595	.2126	.1418	.1673
1.0	0	.7091	.4730	.5580
2.0	+0.0330	1.418	.9462	1.1161

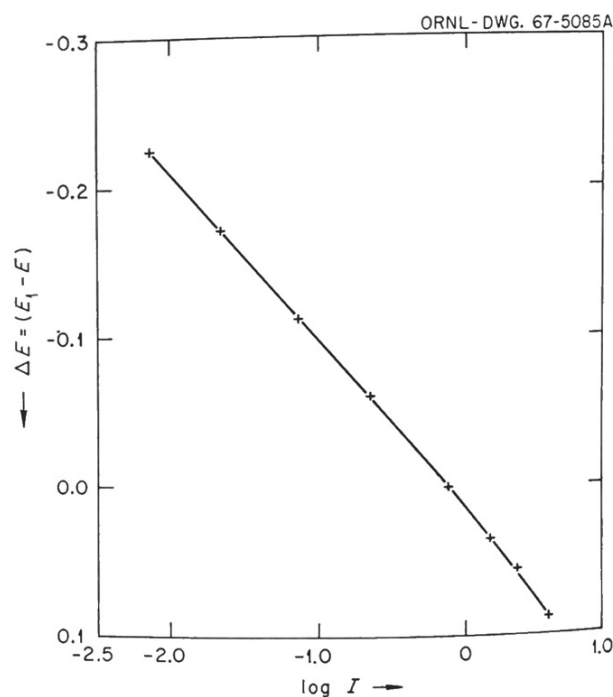


Figure 1. Emf response of cationic glass electrode to concentration of natural sea salt solutions.

Here the  $a$ 's represent the activities of the various ions, the  $k$ 's are empirically determined constants, while  $R$ ,  $T$ , and  $F$  have their usual significance.

Since the pH of the solutions was near 7, the concentration of  $H^+$  was always some five orders of magnitude smaller than that of  $Na^+$ , under which conditions the effect of  $H^+$  is known to be small. A similar argument should hold for the  $Ag^+$  concentration. The concentration of  $K^+$  is not negligible ( $m_K$  being about

2% of  $m_{\text{Na}}$ ) and  $k_K$  was found to be in the range of 6 to 9 for three glass electrodes (7). However, to a first approximation the activity of  $\text{K}^+$  should vary proportionally to that of  $\text{Na}^+$  and thence the ratios of the two cationic expressions should be approximately equal to  $a_{\text{Na}}/(a_{\text{Na}})_1$ . Thus Equation (1) becomes

$$\Delta E \approx \frac{RT}{F} \ln \frac{m_{\text{Na}} m_{\text{Cl}} \gamma^2}{(m_{\text{Na}} m_{\text{Cl}} \gamma^2)_1} \quad (2)$$

As is customary in the treatment of activity coefficient (or osmotic coefficient) data (see e.g., refs. 9, 10) the logarithm of the mean activity coefficient was assumed to be represented by a Debye-Huckel expression plus a (quadratic) power series in ionic strength:

$$\ln \gamma = -\frac{S\sqrt{I}}{1+A\sqrt{I}} + BI + CI^2 \quad (3)$$

where  $S$  is the Debye-Huckel limiting slope and  $A$ ,  $B$ , and  $C$  are adjustable parameters.

Equation (3) was inserted into equation (2) for both  $\ln \gamma$  and  $\ln \gamma_1$ . The parameters  $B$  and  $C$  were then evaluated by the method of least squares for a range of values of  $A$  (1.0, 1.25, 1.5, 1.75 and 2.0) by using the values of  $\Delta E$ ,  $I$ ,  $m_{\text{Na}^+}$  and  $m_{\text{Cl}^-}$  shown in Table I. Although the activity coefficients calculated from the parameters of fit obtained with  $A = 1.5$ , 1.75 and 2.0 were probably all within experimental error (i.e., they were within 1% of each other), the variance of fit was smallest for both the natural and synthetic sea salt solutions when  $A = 2.0$ . These values of the parameters are shown in Table II. The  $B$  and  $C$  parameters

TABLE II

PARAMETERS OF EQUATION (3) FOR SEA SALT SOLUTIONS

	Natural	Synthetic
A =	2.00	2.00
B =	0.13404	0.23072
C =	-0.011735	-0.066470

are very strongly correlated, i.e., if one is changed by a substantial amount a new value of the other one can be obtained which will give an almost equally good fit. Thus although the curves for activity coefficients in natural and synthetic sea salt solutions (Fig. 2) lie close together the values of the parameters (obtained by the method of least squares) are appreciably different.

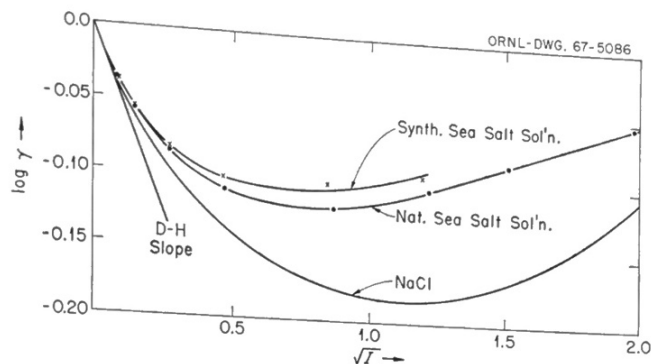


Figure 2. Approximate logarithm of activity coefficient of NaCl vs square root of ionic strength in sea salt conditions.

A plot of  $\log \gamma$  for natural sea salt solutions vs the square root of ionic strength is shown in Figure 2. The corresponding curve for pure NaCl and the Debye-Huckel limiting slope for a 1-1 electrolyte are also shown for comparison. Apparently  $\gamma_{\text{NaCl}}$  in a sea salt mixture deviates from unity by a somewhat smaller amount than it does in pure NaCl solutions.

Values of  $\log \gamma_{\text{NaCl}}$  in synthetic sea water are also shown in Fig. 2. These activity coefficients are larger than those in natural sea salt solutions, with a maximum difference of about 3.5%. The difference between the measurements in natural and synthetic sea salt solutions may be due to the difference in the two media or to the presence of a small amount of bromide in natural sea salt, as well as perhaps some experimental error.

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## LITERATURE CITED

1. M. H. Lietzke and R. W. Stoughton, *This Journal*, **42**, 26 (1967).
2. P. B. Hostetler, A. H. Truesdell and C. L. Christ, *Science*, **155**, 1537 (1967).
3. R. D. Lanier, *J. Phys. Chem.* **69**, 2697, 3992 (1965).
4. C. A. Bower, *Proc. Soil Sci. Soc. Am.* **23**, 29 (1959).
5. T. A. Taulli, *Anal. Chem.* **32**, 186 (1960).
6. K. S. Spiegler, "Salt Water Purification," Wiley, New York (1962).
7. R. D. Lanier, *J. Phys. Chem.* **69**, 2697 (1965).
8. G. Scatchard, *J. Am. Chem. Soc.* **75**, 2883 (1953).
9. M. H. Lietzke and R. W. Stoughton, *J. Phys. Chem.* **65**, 508 (1961).
10. M. H. Lietzke and R. W. Stoughton, *J. Chem. Eng. Data* **12**, 101 (1967).