

# YALE PEABODY MUSEUM

P.O. BOX 208118 | NEW HAVEN CT 06520-8118 USA | PEABODY.YALE. EDU

## JOURNAL OF MARINE RESEARCH

The *Journal of Marine Research*, one of the oldest journals in American marine science, published important peer-reviewed original research on a broad array of topics in physical, biological, and chemical oceanography vital to the academic oceanographic community in the long and rich tradition of the Sears Foundation for Marine Research at Yale University.

An archive of all issues from 1937 to 2021 (Volume 1–79) are available through EliScholar, a digital platform for scholarly publishing provided by Yale University Library at <https://elischolar.library.yale.edu/>.

Requests for permission to clear rights for use of this content should be directed to the authors, their estates, or other representatives. The *Journal of Marine Research* has no contact information beyond the affiliations listed in the published articles. We ask that you provide attribution to the *Journal of Marine Research*.

Yale University provides access to these materials for educational and research purposes only. Copyright or other proprietary rights to content contained in this document may be held by individuals or entities other than, or in addition to, Yale University. You are solely responsible for determining the ownership of the copyright, and for obtaining permission for your intended use. Yale University makes no warranty that your distribution, reproduction, or other use of these materials will not infringe the rights of third parties.



This work is licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 4.0 International License.  
<https://creativecommons.org/licenses/by-nc-sa/4.0/>



# Journal of Marine Research

---

Volume 23, Number 2

## *The Activity Coefficient of Sodium Chloride in Seawater*<sup>1</sup>

R. F. Platford

*Fisheries Research Board of Canada  
Atlantic Oceanographic Group  
Bedford Institute of Oceanography  
Dartmouth, Nova Scotia*

---

### ABSTRACT

Using a sodium amalgam and silver-silver chloride electrode pair, the mean activity coefficient of sodium chloride in synthetic seawater has been compared with that in pure sodium chloride solutions. Effects of concentration and temperature were measured. The mean activity coefficient in synthetic seawater was found to be slightly higher than in a sodium chloride solution of the same ionic strength. No explanation for this is offered.

*Introduction.* Direct measurements of the mean activities of the major ions in seawater have not been reported in the literature although they are necessary if thermodynamic ion association constants are to be applied to seawater (Garels and Thompson 1962). Since the two major ions in seawater are the sodium and chloride ions, it is pertinent to examine methods of measuring the activity,  $a_{\text{Na}^+ + \text{Cl}^-}$ , of sodium chloride in aqueous solutions. The activity,  $a_i$ , of any component in solution is related to its molal concentration,  $m_i$ , by a

1. Accepted for publication and submitted to press 21 January 1965.

quantity called the activity coefficient,  $\gamma_i = a_i/m_i$ . While activity coefficients for ions approach unity in very dilute solutions and can be calculated by existing methods for concentrations up to about 0.1 m (Robinson and Stokes 1959: 230<sup>2</sup>), there appears to be no method for arriving at their values in seawater except by direct measurement.

Boiling-point elevations, freezing-point depressions, diffusion, and electromotive force (EMF) phenomena all depend on activities of solutes in solution and all can be used to measure the activity of pure sodium chloride in aqueous solutions (Robinson 1939, Harned and Owen 1958); however, only EMF measurements that are specific for individual ions are easily applied to multi-component systems such as seawater.

The activity of aqueous sodium chloride has been measured with a flowing sodium amalgam electrode and a silver-silver chloride electrode (Smith and Taylor 1940). It was felt that this electrode pair could also be used to measure the sodium chloride activity in seawater, but with some limitations. The sodium amalgam electrode is specifically responsive to sodium ion activity (Neuhausen 1922), and the silver-silver chloride electrode responds to chloride ion activity if no bromide or iodide is present (Pinching and Bates 1946, Janz 1961). The sodium amalgam electrode must be used in the absence of oxygen.

*Method.* All chemicals, which were "Baker Analyzed Reagent" grade from freshly opened containers, were used without further purification. It was found that sodium chloride fused at red heat in a platinum dish gave the same results as the commercial grade, so the latter was normally used in preparing solutions. Sodium amalgams were prepared by electrolyzing 5% NaOH over a mercury cathode and storing under nitrogen (Smith and Taylor 1940). The amalgams were analyzed by decomposing with hot water and titrating with hydrochloric acid. Since the actual amalgam concentrations did not enter into the final calculations, they are not reported here.

Synthetic seawater was prepared as described by Lyman and Fleming (1940), but some minor constituents included by them were omitted for the present work. The omitted constituents, including bromide and iodide salts, would have contributed less than 0.4% to the ionic strength of the seawater; therefore their effect on the measured activity of sodium chloride can be ignored. The prepared seawater had the following composition: 0.4240 m NaCl, 0.0553 m MgCl<sub>2</sub>, 0.0291 m Na<sub>2</sub>SO<sub>4</sub>, 0.0105 m CaCl<sub>2</sub>, 0.0094 m KCl. This seawater had a salinity of 34.80 g/kg, a sodium-ion molality of 0.4822, and a chloride-ion molality of 0.5650. Lower salinities were prepared by diluting this seawater with distilled water. The chloride ion concentration was checked by titrating with standard silver nitrate. According to the manufacturer's specifica-

2. This book, on pages 174-252, contains a good treatment of the measurement and significance of activity coefficients.

tions, not enough bromide or iodide was present as impurities in the chemicals to affect the silver-silver chloride electrode.

The cell assembly is shown in Fig. 1. The silver-silver chloride electrodes were supplied by Radiometer and were electrolytically coated. Electrical contact with the flowing amalgam was made through a platinum wire sealed in

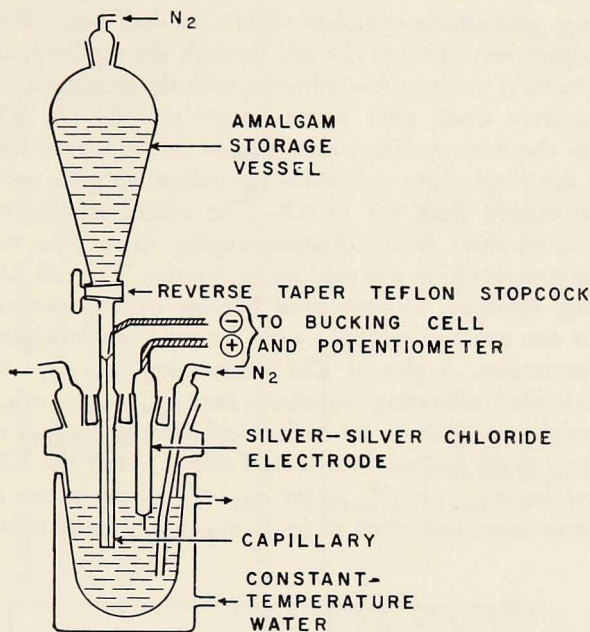


Figure 1. Cell Assembly.

the wall of the capillary. The cell had a small vent above this capillary to prevent suck-back of test solution after the amalgam flow was stopped. The cell voltage was measured with a Radiometer Model 4 pH meter. Since the cell gave an EMF of about 2 volts and since the pH meter had an upper measuring limit of 1.5 volts, it was necessary to buck out part of the cell voltage with a constant voltage from an Epply standard cell. The standard cell voltage, 1.0192 volt, remained constant within 0.1 mv during the measurements. The actual test-cell voltages are not reported here; they depended on both sodium amalgam concentration and sodium chloride activity and therefore varied from run to run. Several runs at different amalgam concentrations ranging from 0.01% to 0.08% sodium by weight were made, the cell being calibrated with sodium chloride solutions for each run, as described below.

Tempered water was circulated through the cell jacket with a Haake Model F constant-temperature circulator. The temperature in the cell was

good to  $\pm 0.2^\circ\text{C}$ , except for the  $0^\circ\text{C}$  run (ice bath), when the temperature was good to  $\pm 0.5^\circ\text{C}$ .

The following procedure was adopted for making measurements. Nitrogen saturated with water vapor was bubbled for five minutes through a sodium chloride solution of known molality in the cell, and the silver-silver chloride electrode was then allowed to equilibrate for one hour; separate tests indicated that equilibrium was usually complete within one-half hour. Following equilibration, amalgam was run into the cell through the capillary, and the EMF was measured within the next few minutes, with the amalgam flowing. When measurements were made after much longer periods, the EMF changed slightly due to the decomposition of amalgam to produce sodium ions. The measurement described above was made for sodium chloride solutions having molalities that ranged from 0.1 to 0.8. The measurements were repeated, using synthetic seawater with salinities ranging from 5‰ to 35‰; the same amalgam concentration was used for each series. The cell EMF increased with increasing amalgam concentration because of the increase in sodium activity, but it was constant within 0.5 mv for any given amalgam and sodium chloride concentration. A plot of EMF versus  $\log a_{\text{Na}^+} + a_{\text{Cl}^-}$  was made for the sodium chloride "calibrating" solutions; here  $a_{\text{Na}^+} + a_{\text{Cl}^-} = m_{\text{NaCl}}^2 (\gamma_{\pm})_{\text{NaCl}}^2$ . The mean activity coefficients for sodium chloride,  $(\gamma_{\pm})_{\text{NaCl}}$ , were obtained from Robinson (1939) and are shown in Table 1. After the EMF had been plotted against  $\log m_{\text{NaCl}}^2 (\gamma_{\pm})_{\text{NaCl}}^2$  (or  $a_{\text{Na}^+} + a_{\text{Cl}^-}$ ), the values of the EMF for the seawater were converted to  $(a_{\text{Na}^+} + a_{\text{Cl}^-})_{\text{sw}}$ , as shown in Fig. 2. The

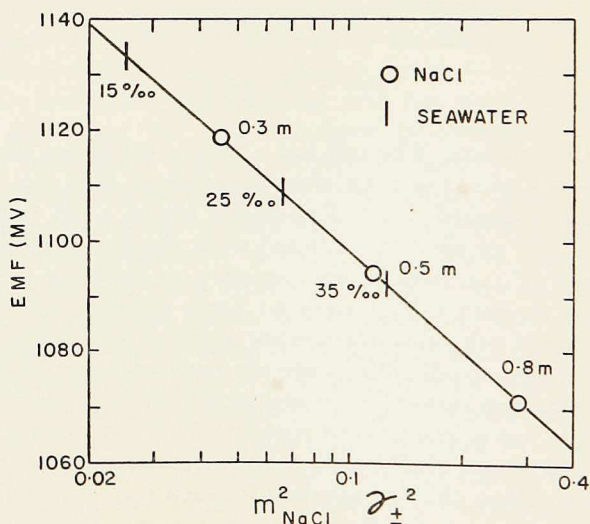


Figure 2. Typical plot of EMF versus  $m_{\text{NaCl}}^2 \gamma_{\pm}^2$ , using 0.06% amalgam.

TABLE I. ACTIVITY COEFFICIENTS AND ACTIVITIES OF SODIUM CHLORIDE IN AQUEOUS SOLUTION (FROM ROBINSON 1939).

$m_{\text{NaCl}}$	0°C		15°C		25°C		35°C	
	$\gamma_{\pm}$	$m^2 \gamma_{\pm}^2$	$\gamma_{\pm}$	$m^2 \gamma_{\pm}^2$	$\gamma_{\pm}$	$m^2 \gamma_{\pm}^2$	$\gamma_{\pm}$	$m^2 \gamma_{\pm}^2$
0.1 .....	0.781	0.00610	0.780	0.00608	0.778	0.00605	0.776	0.00602
0.3 .....	0.705	0.0447	0.707	0.0450	0.708	0.0452	0.707	0.0450
0.5 .....	0.672	0.1130	0.678	0.1150	0.681	0.1160	0.682	0.1162
0.7 .....	0.654	0.210	0.662	0.2145	0.667	0.218	0.669	0.219

TABLE II. MEAN ACTIVITY COEFFICIENT OF SODIUM CHLORIDE IN SYNTHETIC SEAWATER AND IN AQUEOUS SODIUM CHLORIDE.

Salinity ‰	$\gamma_{\text{Seawater}}^{\dagger}$			$\gamma_{\text{NaCl}}^*$	
	Temperature °C	$\mu$	$(\gamma_{\pm})_{sw}$	$m$	$(\gamma_{\pm})_{\text{NaCl}}$
34.8 .....	25	0.72	0.672 ± 0.007	0.72	0.664
25 .....	25	0.52	0.690 ± 0.010	0.52	0.676
15 .....	25	0.31	0.730 ± 0.010	0.31	0.704
5 .....	25	0.10	0.795 ± 0.010	0.10	0.778
34.8 .....	35	0.72	0.685 ± 0.007	0.72	0.666
34.8 .....	25	0.72	0.672 ± 0.007	0.72	0.664
34.8 .....	15	0.72	0.679 ± 0.007	0.72	0.660
34.8 .....	0	0.72	0.650 ± 0.007	0.72	0.653

† Measured.

\* After Robinson 1939.

mean activity coefficient of the sodium chloride in seawater,  $(\gamma_{\pm})_{sw}$ , was then given by the expression

$$(\gamma_{\pm})_{sw} = \left( \frac{(a_{Na^+} + a_{Cl^-})_{sw}}{(m_{Na^+} + m_{Cl^-})_{sw}} \right)^{\frac{1}{2}}.$$

*Results.* The results are shown in Table II and in Figs. 3 and 4. For comparison, the mean activity coefficient of a sodium chloride solution of the same ionic strength,  $\mu$ , as that of seawater is shown in Fig. 3. Each result is the mean of at least four determinations and is shown with its standard deviation. The published values for  $(\gamma_{\pm})_{NaCl}$  appear precise enough so that they contribute a negligible error to the over-all results.

Since Neuhausen (1922) has suggested that ions below sodium in the electromotive series might interfere with the sodium amalgam electrode by forming mixed amalgams, this effect was checked by adding magnesium salts to sodium chloride solutions and by measuring the EMF of the cell (magnesium was the only possible source of trouble, as calcium and potassium are both above sodium in the electromotive series). Solutions of 0.05 m  $MgCl_2$  or 0.05 m  $MgSO_4$  in 0.5 m NaCl gave the same EMF as solutions of 0.5 m NaCl when EMFs from the  $MgCl_2$  solution had been corrected for the presence of additional chloride ion and when both had been corrected for the slight lowerings in the activity coefficient of the sodium chloride caused by the presence of additional salts in the solutions. This indicated that the sodium amalgam electrode was, in fact, reacting specifically with the sodium ions in the synthetic seawater.

The average partial molal heat content,  $\bar{L}_2$ , of the sodium chloride in seawater was estimated from Fig. 4, using the expression (Harned and Owen

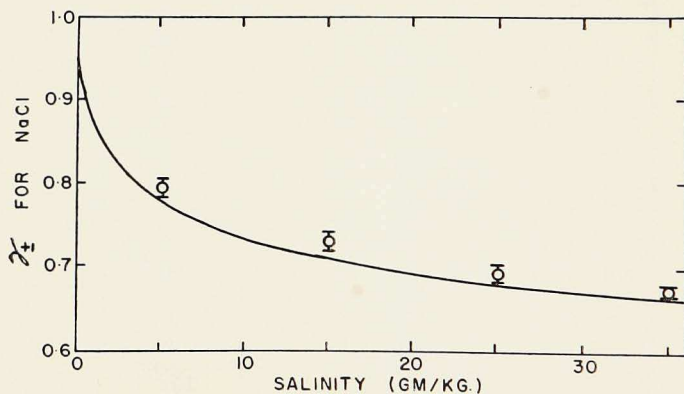


Figure 3. Mean activity coefficient of sodium chloride in seawater as a function of salinity at 25°C (circle with extensions). Mean activity coefficient of pure sodium chloride of the same ionic strength as that of seawater (solid line).

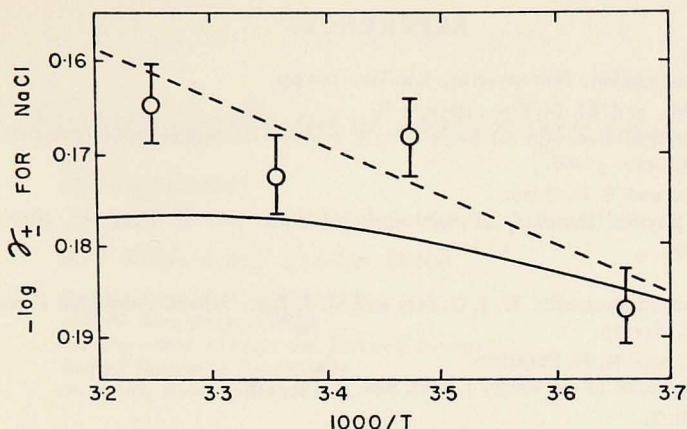


Figure 4. Mean activity coefficient of sodium chloride in seawater as a function of temperature (circle with extensions). Least-squares fit of data (dashed line). Mean activity coefficient of 0.72 m NaCl (solid line).

1958):  $[\partial \ln(\gamma_{\pm})_{sw}]/[\partial(1/T)] = \bar{L}_2/\nu R$ , where  $T$  is the absolute temperature,  $\nu$  is the number of ions per NaCl molecule (i.e., 2), and  $R$  is the gas constant. The value for  $\bar{L}_2$  was about  $-500$  cal/mole.

*Discussion.* The mean activity coefficient of sodium chloride in seawater is slightly higher than that of a sodium chloride solution of the same ionic strength as the seawater. The partial molal heat content of the sodium chloride is also higher than that in aqueous sodium chloride, especially at the higher temperatures; however, the difference is not great (Fig. 4), considering the experimental error in the present work. It appears that the behavior of sodium chloride in seawater is similar to that in a pure sodium chloride solution; the general practice of assuming that the activity coefficient of a salt in seawater is given by that of the pure salt solution of the same ionic strength is a good approximation in the case of sodium chloride. This is reasonable, since sodium chloride contributes about 70% to the ionic strength of seawater.

It is known that no ion pairs exist in a sodium chloride solution (Davies 1962: 169) and it is unlikely that any large fraction of either sodium or chloride ions in seawater form pairs with other ions in view of the close similarity between  $(\gamma_{\pm})_{NaCl}$  and  $(\gamma_{\pm})_{sw}$ ; otherwise one would expect  $(\gamma_{\pm})_{sw}$  to be less than  $(\gamma_{\pm})_{NaCl}$  by an amount depending on the extent of ion-pair formation.



## REFERENCES

- DAVIES, C. W.  
1962. Ion association. Butterworths, London. 190 pp.
- GARRELS, R. M., and M. E. THOMPSON  
1962. A chemical model for sea water at 25°C and one atmosphere total pressure. *Amer. J. Sci.*, 260: 57-66.
- HARNED, H. S., and B. B. OWEN  
1958. The physical chemistry of electrolytic solutions. 3rd. ed. Reinhold, New York. 803 pp.
- JANZ, G. J.  
1961. Reference electrodes. D. J. G. Ives and G. J. Janz, editors. Academic Press, New York. 651 pp.
- LYMAN, JOHN, and R. H. FLEMING  
1940. Composition of sea water. *J. Mar. Res.* 3: 134-146.
- NEUHAUSEN, B. S.  
1922. A study of the sodium amalgam electrode for the determination of sodium ion. *J. Amer. chem. Soc.*, 44: 1411-1416.
- PINCHING, G. D., and R. G. BATES  
1946. Purification of sodium chloride and potassium chloride for use in electrochemical work, and the determination of small amounts of bromide. I. Effect of dissolved impurities on the potentials of silver-silver halide electrodes immersed in solutions of alkali salts. *J. Res. nat. Bur. Stand.*, 37: 311-319.
- ROBINSON, R. A.  
1939. The heat content and heat capacity of sodium chloride solutions. *Trans. Faraday Soc.*, 35: 1222-1228.
- ROBINSON, R. A., and R. H. STOKES  
1959. Electrolyte solutions. Butterworths, London. 559 pp.
- SMITH, E. R., and J. K. TAYLOR  
1940. Standard electrode potential of sodium. *J. Res. nat. Bur. Stand.*, 25: 731-746.