ON THE CHANGE IN ELECTRICAL CONDUCTANCE OF SEAWATER WITH TEMPERATURE[1]

Peter K. Weyl
Department of Oceanography, Oregon State University, Corvallis

ABSTRACT

A comparison of the measurements of the specific conductance of seawater by Thomas, Thompson, and Utterback and of sodium chloride solutions by Bremner, Thompson, and Utterback shows that the temperature dependence of the two are essentially the same. The data are consistent with those of Gheorghiu and Calinicenco, but their conclusion that the temperature coefficient of conductance of seawater is measurably greater than that of sodium chloride solutions is in error.

INTRODUCTION

With the widespread use of the electrical conductance salinometer, the data on the temperature dependence of conductance have taken on new importance. In a review, Richards (1957) refers to work by Gheorghiu and Calinicenco (1940) whose "findings are not in agreement with those of Thomas et al. (1934)." In particular, the third conclusion of Gheorghiu and Calinicenco states that "one can explain the fact that the temperature coefficient of conductance of sea water is appreciably greater than that of NaCl of the same concentration, by the hydrolysis of sea water." In view of these statements, it is worthwhile to reexamine critically the data on seawater and sodium chloride conductance.

THE TEMPERATURE DEPENDENCE OF THE ELECTRICAL CONDUCTANCE OF SEAWATER

The data on the electrical conductance of seawater have been reviewed critically by Pollak (1954). He points out that the data of Thomas, Thompson, and Utterback are inaccurate for the following reasons: 1) the value for the conductance of their reference KCl solution was slightly in error; 2) the conductance cell they used was subject to slight systematic errors. Nevertheless, these data remain the best available.

Pollak did not examine the data of Gheorghiu and Calinicenco (1940). However, it is clear that their data do not compare in accuracy with those of Thomas et al. (1934). It is best, therefore, to analyze the latter data and then to determine whether the former are consistent with them.

The specific conductance of seawater (K_s) is a function of the composition of the water, its temperature, and pressure. The effect of pressure on conductance has recently been investigated by Horne and Frysinger (1963). We will limit ourselves to measurements at one atmosphere pressure. As a first approximation, the composition of the seawater can be expressed by its chlorinity. The specific conductance then is a function of the two variables, chlorinity (Cl) and temperature (t). Cox et al. (1962) have shown that the specific conductance of seawater at constant chlorinity and temperature may vary somewhat. Fortunately, Thomas et al. (1934) made measurements for the same waters at a number of temperatures. The deviations observed by Cox et al. will have only a second-order effect on the ratio of the specific conductance for the same water measured at different temperatures.

To analyze the ratios of conductances, it is most convenient to work with the logarithms of the data. Choosing 25C as the reference temperature, we introduce a parameter α defined by:

$$\alpha = \frac{\log K_s\,(Cl, t) - \log K_s\,(Cl, 25)}{t - 25}.$$

The values of α obtained from the data of Thomas et al. (1934) are given in Table 1 and plotted in Fig. 1. For any one temperature, a plot of α vs. chlorinity can be ap-

[1] This work was carried out under National Science Foundation Grant GP-2044 and Office of Naval Research Contract Nonr 1286(10) Project NR083-102.

TABLE 1. *Value of logarithmic temperature parameter α for seawater*

	Cl‰	$10^4\alpha$, Deg^{-1}				
		20C	15C	10C	5C	0C
Data of Thomas et al. (1934)	5.147	90.68	94.24	98.29	102.34	107.54
	7.559	90.32	93.64	97.61	101.97	106.95
	10.476	89.82	93.25	97.16	101.38	106.30
	12.063	89.60	92.99	96.75	101.03	105.94
	14.006	89.42	92.80	96.61	100.66	105.56
	16.750	88.92	92.13	96.24	100.29	105.07
	18.998	88.88	92.22	96.10	99.95	104.94
	19.227	88.86	92.14	95.89	99.84	104.46
Empirical Formula	0.000	91.3	94.9	99.0	103.6	108.7
	20.000	88.5	92.0	95.6	99.9	104.3

proximated by a straight line. The lines drawn fit the following empirical expression:

$$10^4\alpha = 88.3 + 0.55\tau + 0.0107\tau^2 - Cl\,‰\,(0.145 - 0.002\tau + 0.0002\tau^2) \quad (1)$$

where $\tau = 25 - t$.

For most of the data, α differs from equation (1) by no more than 0.00002. For 0C, this implies an error of 0.1% in the specific conductance. For temperatures closer to 25C, the error is proportionately less. Now,

$$\log K_s\,(Cl, \tau) = -\tau\alpha + \log K_s\,(Cl, 25)\,. \quad (2)$$

The logarithmic temperature derivative at constant chlorinity then is

$$\frac{\partial \ln K_s\,(Cl, \tau)}{\partial t} = 2.3026\left[\alpha(Cl, \tau) + \tau\frac{\partial \alpha}{\partial \tau}\right] \quad (3)$$

$$= 0.01\,[2.033 + 0.0253\tau + 0.000739\tau^2 - Cl‰\,(0.0033 - 0.000092\tau + 0.0000138\tau^2)]\,.$$

The logarithmic temperature derivative of electrical conductance for seawater of

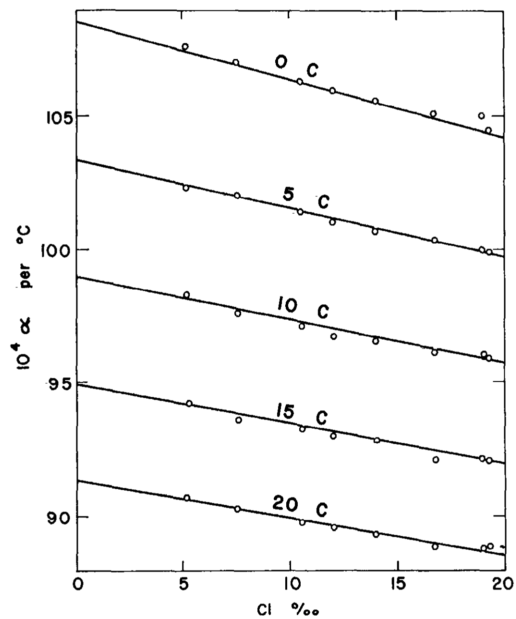

FIG. 1. α for seawater.

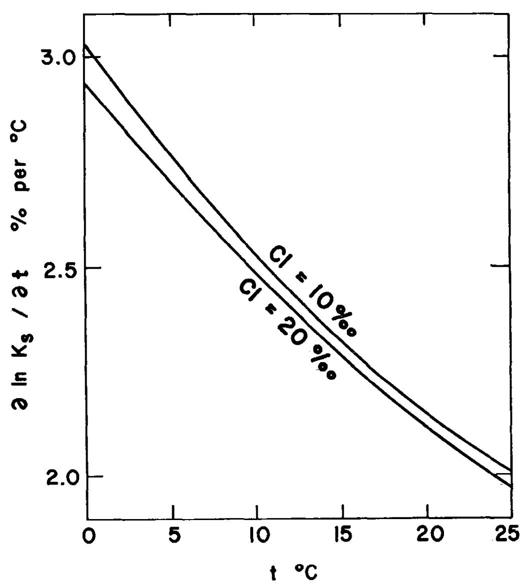

FIG. 2. Logarithmic temperature derivative of the specific conductance of seawater.

chlorinities of 10 and 20‰ is plotted in Fig. 2. It decreases from about 3% per degree at 0C to about 2% per degree at 25C.

Although the data of Gheorghiu and Calinicenco are less accurate than those of Thomas et al., it is still pertinent to inquire if the two sets of data are consistent. We have, therefore, calculated values of the parameter α from the data of Gheorghiu and Calinicenco. Fig. 3 is a plot of these data against temperature together with our empirical curves. The data show considerable scatter, masking the effect of salinity on α.

To calculate the electrical conductance of seawater at any temperature and chlorinity, we can use equation (1) together with an expression for the change in conductance with chlorinity at 25C. One can, of course, use the power series for the conductance given by Thomas et al. (1934). However, an expression for the logarithm of the specific conductance is more useful in conjunction with equation (1). We find that near a chlorinity of 19‰, the following expression fits the data of Thomas et al. with high precision:

$$\log K_s\,(Cl, 25C) = 0.892 \log Cl‰ + 0.57625 \pm 0.00005; \quad 17‰ < Cl < 20‰ . \quad (4)$$

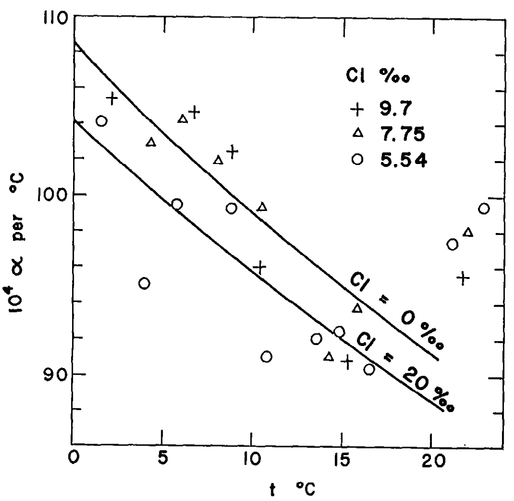

FIG. 3. Comparison of the data of Gheorghiu and Calinicenco (1940) with equation (1).

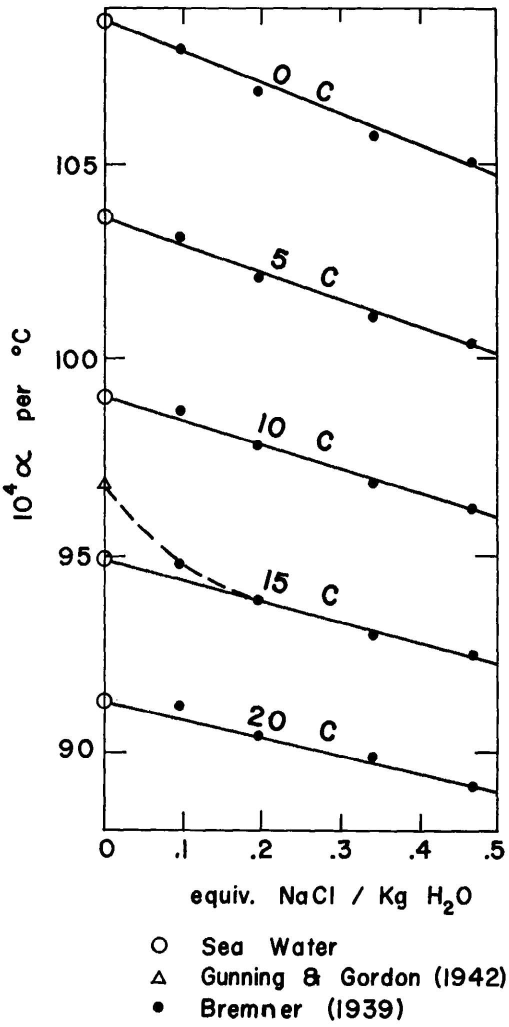

FIG. 4. α for NaCl solutions.

THE TEMPERATURE DEPENDENCE OF THE ELECTRICAL CONDUCTANCE OF SODIUM CHLORIDE SOLUTIONS

The specific conductance of sodium chloride solutions in the concentration and temperature range of interest has been measured by Bremner, Thompson, and Utterback (1939). Treating their data in the same manner as the seawater data, we obtain the values for the logarithmic temperature parameter α shown in Fig. 4 and in Table 2. In Fig. 4, we have also indicated the extrapolated values of α for the seawater of zero chlorinity. These extrapolated seawater data and the data for the sodium

TABLE 2. *Value of the logarithmic temperature parameter α for sodium chloride solutions*

	Mg equivalent / kg H_2O	$10^4\alpha$, Deg^{-1}				
		20C	15C	10C	5C	0C
Data of Bremner et al. (1939)	96.116	91.18	94.73	98.71	103.13	108.01
	193.318	90.38	93.85	97.76	102.08	106.87
	341.198	89.88	93.03	96.84	101.06	105.69
	466.377	89.14	92.48	96.19	100.37	105.00
Empirical Formula	0.0	91.3	94.9	99.0	103.6	108.7
	500.0	89.0	92.3	96.0	101.1	104.7
Gunning and Gordon (1942)	0.0		96.84			

chloride solution fit the following empirical equation:

$$10^4\alpha = 88.3 + 0.55\tau + 0.0107\tau^2 - N\,(4.16 + 0.70\tau + 0.0034\tau^2)\,. \quad (5)$$

The concentrations (N) are in gram equivalents per kg water.

Gunning and Gordon (1942) measured the equivalent conductance of sodium chloride at infinite dilution at 25 and 15C. The value of α obtained from these data is indicated in Fig. 4 and does not fit the empirical lines. We conclude that the extrapolations to zero salinity have no physical significance and that the empirical relationships are not valid for very dilute (less than 0.1 N) solutions. Although there are no data, the same undoubtedly holds for seawater.

CONCLUSIONS

A comparison of Figs. 1 and 4 shows that the temperature dependence of the specific electrical conductance of seawater is similar to that of sodium chloride solutions of comparable concentrations. While a precise comparison is meaningless, the statement of Gheorghiu and Calinicenco that the temperature coefficient for seawater is significantly greater than that for sodium chloride solutions is in error. The fact, pointed out by Richards (1957), that Gheorghiu and Calinicenco gave a linear temperature dependence while Thomas et al. (1934) show a departure from linearity, can be attributed to the lower precision of the former measurements.

The specific conductance of seawater in millimhos per cm over a chlorinity range from 17–20‰ and a temperature range from 0–25C is given by the following empirical equation:

$$\log K_s = 0.57627 + 0.892 \log Cl\,(‰) - 10^{-4}\tau\,[88.3 + 0.55\tau + 0.0107\tau^2 - Cl\,(‰)\,(0.145 - 0.002\tau + 0.0002\tau^2)] \quad (6)$$

where $\tau = 25 - t$C.

Conductances calculated by equation (6) over the range indicated will differ from the measured data by less than 0.1%.

REFERENCES

BREMNER, R. W., T. G. THOMPSON, AND C. L. UTTERBACK. 1939. Electrical conductance of pure and mixed salt solutions in the temperature range 0 to 25°. J. Am. Chem. Soc., **61**: 1219–1223.

COX, R. A., F. CULKIN, R. GREENHALGH, AND J. P. RILEY. 1962. Chlorinity, conductivity and density of sea water. Nature, **193**: 518–520.

GHEORGHIU, V. G., AND N. CALINICENCO. 1940. Étude sur la variation de la conductibilité électrique de l'eau de la Mer Noire avec la température et son emploi a la mesure de la température de l'eau marine. Ann. Sci. Univ. Jassy, **26**(Sect. II): 3–18.

GUNNING, H. E., AND A. R. GORDON. 1942. The conductance and ionic mobilities for aqueous solutions of potassium and sodium chloride at temperatures from 15 to 45C. J. Chem. Phys., **10**: 126–131.

HORNE, R. A., AND G. R. FRYSINGER. 1963. The effect of pressure on the electrical conductivity of sea water. J. Geophys. Res., **68**: 1967–1973.

POLLAK, M. J. 1954. The use of electrical conductivity measurements for chlorinity determinations. J. Marine Res., **13**: 228–231.

RICHARDS, F. A. 1957. Some current aspects of chemical oceanography, p. 77–128. *In* Progress in physics and chemistry of the earth, v. 2. Pergamon Press, London.

THOMAS, B. D., T. G. THOMPSON, AND C. L. UTTERBACK. 1934. The electrical conductivity of sea water. J. Conseil, Conseil Perm. Intern. Exploration Mer, **9**: 28–35.