

**The Conductivity-Density-Salinity-Chlorinity Relationships for Estuarine Waters**



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## NOTES

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### The conductivity-density-salinity-chlorinity relationships for estuarine waters<sup>1</sup>

*Abstract*—The relative conductivity and density of estuarine waters formed by mixing “world” river water with standard seawater have been determined. The results are used to examine the conductivity-density-salinity-chlorinity relationships of estuarine waters of known composition with seawater diluted with pure water (i.e. the new International Equation of State and Practical Salinity Scale). The maximum difference between the true salinity and the value derived from conductivity was 0.047 in dilute solutions; the maximum density difference between the measured and calculated values was  $35 \times 10^{-6} \text{ g}\cdot\text{cm}^{-3}$ . These results are compared with measurements of waters from the St. Lawrence estuary.

The limitations of using the new Practical Salinity Scale (UNESCO 1981*a*) for estuarine waters have been discussed (Parsons 1982; Sharp and Culbertson 1982; Gieskes 1982). The limitations of the conductivity method to determine the salinity or density of seawater solutions have been examined by several workers (e.g. Brewer and Bradshaw 1975; Millero et al. 1976*a,b*, 1978; Millero and Kremling 1976; Poisson et al. 1980, 1981). Studies have also been made to examine the limitations of the International Equation of State of Seawater (UNESCO 1981*b*) for estuarine waters (Millero 1975, 1978; Millero et al. 1976*a,b,c*; Millero and Kremling 1976; Poisson et al. 1980).

I will examine here the limitations of using the Practical Salinity Scale to determine the conductivity-density-salinity-chlorinity relationships for estuarine waters of known composition (Millero et al. 1976*c*).

The composition of the artificial “world” river water (Livingstone 1963) used to make the estuarine mixtures with standard seawater ( $S = 35.013$ ) was the same as used in

an earlier study (Millero et al. 1976*c*). The concentration of river salts was 105.7 g in 1 kg of solution and the chlorinity was 0.008  $\text{g}\cdot\text{kg}^{-1}$ . The seawater solution is assumed to have a composition similar to that of average seawater (Millero 1982). The total grams of salt in 1 kg of estuarine water is related to the chlorinity by

$$g_T(\text{est}) = 0.092 + 1.80271 \text{ Cl} \quad (1)$$

where Cl is the chlorinity (g of halide per kg of solution). The total salinity of these estuarine waters can be determined from  $S_T = g_T/1.00488$  (Millero 1982). Equation 1, thus, becomes

$$S_T = 0.092 + 1.80183 \text{ Cl} \quad (2)$$

The relative conductivities of the estuarine waters were measured on a Guildline Autosol salinometer calibrated with standard seawater and operated at  $24.000^\circ \pm 0.002^\circ\text{C}$ . The densities were measured at  $25.000^\circ \pm 0.002^\circ\text{C}$  with a flow densimeter described in detail elsewhere (Pickler et al. 1974). The densimeter was calibrated with standard seawater and ion-exchanged (Millipore Super Q) water. The densities were precise to  $\pm 3 \times 10^{-6} \text{ g}\cdot\text{cm}^{-3}$  (Millero et al. 1976*c*).

The chlorinities of the samples were determined by weight from the known chlorinities of seawater (19.381) and the river water (0.008). They are thought to be reliable to  $\pm 0.002$ .

The conductivity and density ( $\rho$  and  $\rho^0$  are the densities of solution and water) for the estuarine mixtures are given in Table 1 at various chlorinities. The conductivity ratios ( $R_{24}$ ) at  $24^\circ\text{C}$  were used to estimate the conductivity salinity ( $S_{\text{COND}}$ ) with the 1978 Practical Salinity Scale (see Table 1). These values have been fit to the equation

$$S_{\text{COND}} = 0.044 + 1.803898 \text{ Cl} \quad (3)$$

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Table 1. The conductivity ratio, density, chlorinity and salinity of estuarine waters.

Cl	2R <sub>24</sub>	(ρ - ρ <sup>0</sup> )10 <sup>3</sup>	S <sub>COND</sub>	S <sub>DENS</sub>
19.381	2.00066	26.305	35.013	35.013
17.706	1.84557	24.030	31.982	32.001
15.522	1.64060	21.060	28.042	28.060
13.823	1.47825	18.757	24.975	24.999
11.822	1.28406	16.048	21.372	21.393
9.733	1.07621	13.224	17.596	17.630
7.835	0.88353	10.660	14.176	14.209
5.922	0.68372	8.079	10.721	10.763
3.988	0.47612	5.469	7.243	7.278
2.039	0.25624	2.835	3.722	3.766
1.623	0.20763	2.273	2.973	3.017
1.235	0.16116	1.747	2.271	2.317
0.789	0.10689	1.142	1.470	1.513
0.417	0.05975	0.637	0.798	0.843
0.008	0.00443	0.079	0.059	0.105

Table 2. Calculation of the infinite dilution equivalent conductance of various waters at 25°C.

Ion	Λ <sup>0</sup> †	E <sub>i</sub> Λ <sup>0*</sup>		
		Seawater	World river water	St. Lawrence River
Ca <sup>2+</sup>	59.51	46.97	31.41	35.40
Mg <sup>2+</sup>	53.50	9.32	12.71	13.15
Na <sup>+</sup>	50.10	38.71	9.67	7.24
K <sup>+</sup>	73.50	1.24	3.06	0.91
HCO <sub>3</sub> <sup>-</sup>	44.50	0.14	29.79	25.19
SO <sub>4</sub> <sup>2-</sup>	89.02	7.46	13.14	13.89
Cl <sup>-</sup>	76.35	68.77	11.83	18.61
NO <sub>3</sub> <sup>-</sup>	71.46	0.20‡	0.81	—
Λ <sup>0</sup> =		127.85§	112.42§	114.41§

\* E<sub>i</sub> is the equivalent function of species *i* using the composition data of Millero (1982) for seawater, Millero et al. (1976c) for world river water, and Poisson et al. (1980) for St. Lawrence River water.  
 † From Robinson and Stokes 1965.  
 ‡ From Sr<sup>2+</sup>, F<sup>-</sup>, Br<sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and B(OH)<sub>4</sub><sup>-</sup> (see Millero 1975).  
 § Λ<sup>0</sup> = Σ E<sub>i</sub> Λ<sup>0</sup>.

which has a σ = 0.004. A slightly better fit is obtained at higher chlorinities (17–19) if a second-degree equation is used; however, it is not statistically justified. The larger deviations between Cl = 17–19 are probably related to the experimental errors due to manipulation of the samples at higher concentrations (i.e. evaporation and errors in weighing).

The measured densities of the estuarine samples were used to calculate the salinity (S<sub>DENS</sub>) by iteration, using the International Equation of State of Seawater (Millero and Poisson 1981). The density-derived salinities have been fit to the equation

$$S_{DENS} = 0.092 + 1.80186 Cl \quad (4)$$

which has a σ = 0.002. The differences in

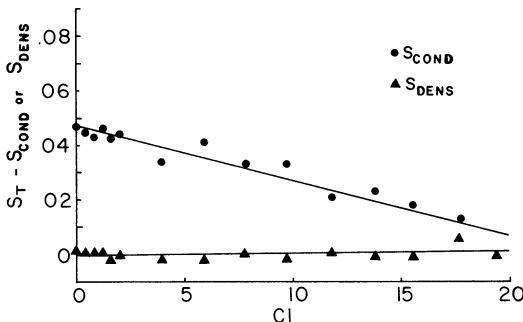


Fig. 1. The differences between the true salinity (S<sub>T</sub>) and the values determined from conductivity (S<sub>COND</sub>) and density (S<sub>DENS</sub>) for artificial estuarine waters as a function of chlorinity.

the true or absolute (S<sub>T</sub>) salinity of the estuarine waters (Eq. 2) and the values determined from conductivity and density measurements are shown in Fig. 1.

The salinities derived from conductivity show a linear offset from the true salinity

$$\Delta S = S_T - S_{COND} = 0.048 - 0.00204 Cl \quad (5)$$

The salinities derived from density are in agreement with the true salinity as found in previous work (Millero et al. 1976c).

The lower values of S<sub>COND</sub> than of S<sub>T</sub> are related to the different equivalent conductances of the major components of seawater and world river water. The conductivities of Na<sup>+</sup> and Cl<sup>-</sup> are larger than Mg<sup>2+</sup>, Ca<sup>2+</sup>, and HCO<sub>3</sub><sup>-</sup> (Robinson and Stokes 1965); thus, at a given chlorinity the conductivity of seawater diluted with pure water is greater than that of estuarine waters. In dilute solutions below Cl = 2.0, my results indicate that the conductivity of river water is 0.94 ± 0.02 times lower than seawater diluted to the same Cl. This can be compared to a value of Λ<sup>0</sup><sub>RW</sub>/Λ<sup>0</sup><sub>SW</sub> = 0.88 calculated (Table 2) from infinite dilution conductivity data (Millero 1975; Poisson et al. 1979; Robinson and Stokes 1965). Part of the difference between the calculated and measured ratio is related to the limitation of the Practical Salinity Scale to S = 2.000

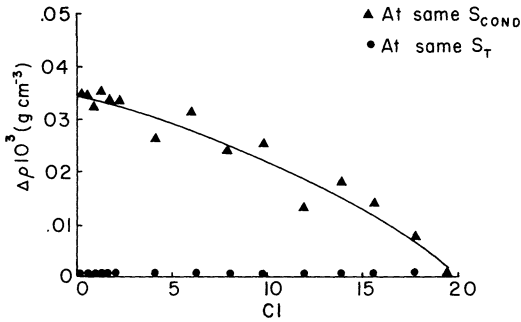


Fig. 2. The differences between the measured and calculated densities at the same  $S_{\text{COND}}$  and  $S_T$  for artificial estuarine waters as a function of chlorinity.

(UNESCO 1981a). The scale can be extended to lower salinities by replacing the  $a_0$  term with

$$a_0 = 0.0080(r + r^2)/[1 + (r + r^2)] \quad (6)$$

where  $r = R_{15}/0.0032$  (Dauphinee et al. 1980).

My results indicate that it is possible to make reasonable estimates of the ratio of the true salinity to the conductivity salinity if the composition of the river end member is known (*see also* Poisson et al. 1979). Since this is not always possible, it may be necessary to determine the relationship by doing mixing experiments in the laboratory. Since many salinometers do not yield reliable conductivities in dilute solutions, it is important to use seawater diluted with water to calibrate a given salinometer before using it to measure estuarine samples. The Practical Salinity Scale makes this calibration accurate to very dilute solutions, if Eq. 6 is used.

Since one of the reasons for measuring the salinity is frequently to determine a physical property, it is interesting to examine the errors involved in using  $S_{\text{COND}}$  to determine the density of estuarine waters. A comparison of the measured and calculated densities using the International Equation of State is shown in Fig. 2. The maximum differences are  $35 \times 10^{-6} \text{ g} \cdot \text{cm}^{-3}$  near the river end member. As shown elsewhere (Millero et al. 1976c) and in Fig. 2, these differences are within  $\pm 3 \times 10^{-6} \text{ g} \cdot \text{cm}^{-3}$ , if the comparisons are made at the same true

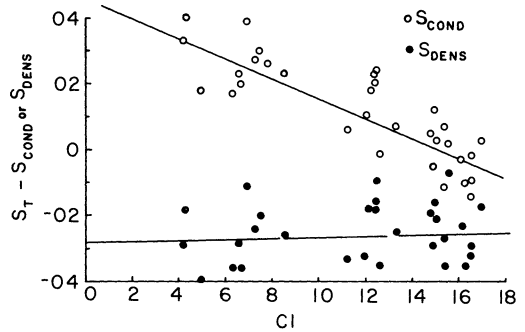


Fig. 3. The differences between the true salinity ( $S_T$ ) and the values determined for conductivity ( $S_{\text{COND}}$ ) and density ( $S_{\text{DENS}}$ ) for St. Lawrence estuarine waters (Poisson et al. 1980) as a function of chlorinity.

salinity. Salinities derived from the density will be reliable only when the river salts have an effect on the density similar to that of sea salts. This is true for average river water (Millero 1975), but may not be the case for every river (Poisson et al. 1980). St. Lawrence River waters, for example, have a predicted density that is  $14 \times 10^{-6} \text{ g} \cdot \text{cm}^{-3}$  higher than that of seawater diluted to the same chlorinity.

It is interesting to compare our model results to real estuarine waters. Since conductivity measurements on the Practical Salinity Scale have not been made for many estuarine waters, it is only possible at present to examine the St. Lawrence estuarine system (Poisson et al. 1980). Values of the true salinity for these waters can be estimated from the equation

$$S_T = 0.131 + 1.78982 \text{ Cl} \quad (7)$$

which is based on a linear mixing model (Poisson et al. 1980).

From the experimental density and conductivity measurements of Poisson et al. (1980) I have determined  $S_{\text{COND}}$  and  $S_{\text{DENS}}$  using the Practical Salinity Scale and the International Equation of State (UNESCO 1981a,b). The results have been fit to the equations

$$S_{\text{COND}} = 0.084 + 1.8028 \text{ Cl}, \quad (8)$$

and

$$S_{\text{DENS}} = 0.159 + 1.7996 \text{ Cl}, \quad (9)$$

which have values of  $\sigma = 0.008$  and  $0.009$ .

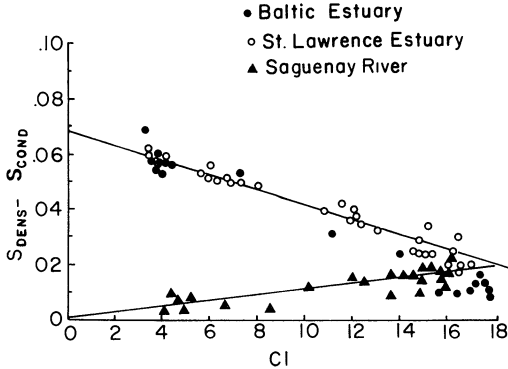


Fig. 4. The differences between the salinity derived from density ( $S_{\text{DENS}}$ ) and conductivity ( $S_{\text{COND}}$ ) for various estuarine waters as a function of chlorinity.

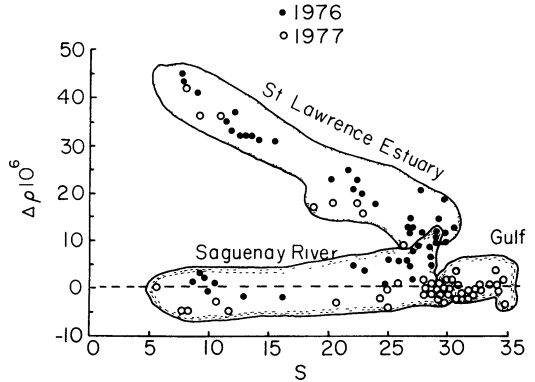


Fig. 5. The differences between the measured and calculated densities for St. Lawrence estuarine waters as a function of salinity.

The differences between  $S_T$  and  $S_{\text{COND}}$  or  $S_{\text{DENS}}$  are shown in Fig. 3. Since values of  $S_T$  cannot be determined for the Saguenay River (part of the St. Lawrence system), it is not possible to make similar comparisons for these waters.

Although there is some scatter in the data, the differences between  $S_T$  and  $S_{\text{COND}}$  appear to be linear and approach values of 0.02–0.04 in dilute solutions similar to our model results. From composition data for the river end member (Poisson et al. 1980) and infinite dilution conductance data (Robinson and Stokes 1965), I calculate a theoretical value of  $S_T/S_{\text{COND}} = \Lambda^0_{\text{RW}}/\Lambda^0_{\text{SW}} = 0.89$  (see Table 2), which gives a value of  $S_T - S_{\text{COND}} = 0.02$ , in reasonable agreement with the extrapolated value.

The values of  $S_T - S_{\text{DENS}}$  for the St. Lawrence waters are negative ( $-0.03 \pm 0.01$ ) over the entire chlorinity range. Part of this difference in dilute solutions is related to the density difference between St. Lawrence River water and seawater diluted to the same chlorinity ( $14 \times 10^{-6} \text{ g} \cdot \text{cm}^{-3}$ ). The linear offset could also be caused by the presence of a dissolved nonelectrolyte of similar concentration in the entire estuarine system. The negative values of  $S_T - S_{\text{COND}}$  and  $S_T - S_{\text{DENS}}$  at high chlorinities cannot be related to the river end member and may be caused by differences in the composition of the St. Lawrence seawater end member and average seawater. This is more clearly demonstrated in Fig. 4 where the differences

between  $S_{\text{DENS}}$  and  $S_{\text{COND}}$  are given for the St. Lawrence and the Saguenay River estuarine systems. At high chlorinities the differences approach 0.02 instead of zero. These results can be contrasted with those for the Baltic estuarine system (Millero and Kremling 1976; Millero 1978), which can be represented by mixing average seawater with Baltic river waters.

The divergence of the seawater end member in the St. Lawrence system is more clearly demonstrated when one compares the differences in the density measured and calculated from the International Equation of State using  $S_{\text{COND}}$ . These results are shown in Fig. 5. For the Saguenay River and the Gulf of St. Lawrence (Poisson et al. 1980) the measured densities agree with seawater-diluted values to  $\pm 10 \times 10^{-6} \text{ g} \cdot \text{cm}^{-3}$ . The 1976 results at high salinities for the St. Lawrence and Saguenay Rivers show deviations as high as  $20 \times 10^{-6} \text{ g} \cdot \text{cm}^{-3}$ .

The extrapolated deviation for low salinities are  $\approx 50 \times 10^{-6} \text{ g} \cdot \text{cm}^{-3}$ , which is higher than found for the artificial estuary results discussed earlier. The expected values from  $S_T - S_{\text{COND}} = 0.04$  at  $\text{Cl} = 0$  is  $\approx 35 \times 10^{-6} \text{ g} \cdot \text{cm}^{-3}$ , if the river salts have the same effect on the density as seawater or our artificial estuarine system. As stated earlier, the extra 15 ppm difference ( $50 - 35 \times 10^{-6} \text{ g} \cdot \text{cm}^{-3}$ ) is related to the volume properties of the component ions of the St. Lawrence River waters.

These results indicate that, although dilute St. Lawrence River waters have a conductivity similar to world river waters, the densities are different. Thus, for careful estuarine work it is necessary to measure both density and conductivity as a function of chlorinity to fully characterize the system. If errors of  $\pm 0.04$  in salinity and  $\pm 50 \times 10^{-6} \text{ g} \cdot \text{cm}^{-3}$  can be tolerated, the Practical Salinity Scale (UNESCO 1981a) and the International Equation of State of Seawater (UNESCO 1981b) can be used for estuarine systems without a knowledge of the detailed ionic composition.

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