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Effect of pressure on the partial equivalent volume of salts in seawater

by Alvin Bradshaw¹ and Karl E. Schleicher¹

ABSTRACT

The effect of pressure on the partial equivalent volumes of salts of the major ions in 35‰ seawater at 10 and 25°C was determined for applied pressures of 400 and 1000 bars from measurements of the change in solution compression with salt concentration. Partial equivalent compressibilities at atmospheric pressure ($\bar{\kappa}_e$) were derived from these results and were compared, where data exist, with the values of others in 0.725 m NaCl solution. In all cases, the present partial equivalent compressibilities were in absolute value less than or equal to these. The largest differences were found in the comparisons with the theoretical estimates of Owen and Brinkley (1941) at 25°C. With the exception of NaNO₃ and Ca(NO₃)₂ at 25°C, the smallest differences ($|\delta\bar{\kappa}_e| \leq 5 \times 10^{-4}$ cm³/equivalent/bar) were found for values from the results of Millero (1982a), Chen *et al.* (1977) and Millero *et al.* (1974): the larger differences in the cases of the two exceptions are believed to be due to larger than average experimental errors in the present data; recalculation of the present values on the assumption that the compression varies linearly with concentration over the measurement range increases their precision and reduces the differences for all salts to $|\delta\bar{\kappa}_e| \leq 4 \times 10^{-4}$ cm³/equivalent/bar.

1. Introduction

The partial volume \bar{V}_i of a component i of a solution of volume V is defined by

$$\bar{V}_i = \left. \frac{\partial V}{\partial q_i} \right|_{T, P, q_{j \neq i}} \quad (1)$$

where T and P are temperature and pressure, and q_j are quantities of the components. Units of gram, equivalent and mole give \bar{V}_i as partial specific, partial equivalent and partial molal volume.

Partial volumes in seawater have practical and theoretical uses in physical and chemical oceanography. For example:

1) They satisfy the equation

$$V = \sum_j q_j \bar{V}_j \quad (2)$$

and hence can be used to construct a theoretical density (or specific volume) equation, as was done by Wirth (1940) at atmospheric pressure, or to predict density deviations due to anomalies in composition (Conners and Weyl, 1968; Brewer and Bradshaw, 1975).

2) Partial molal volumes can be used to predict the pressure effect on equilibrium constants (K) through the thermodynamic equation (seawater reference state)

$$-RT \frac{\partial \ln K}{\partial P} = \sum \bar{V}_{\text{products}} - \sum \bar{V}_{\text{reactants}} \quad (3)$$

The equation is exact only for completely specified reactions; errors can occur, for example, when ion complexing of the components of the reaction with other components of the seawater medium are ignored.

The partial equivalent or partial molal volumes of the major salts in seawater at atmospheric pressure were measured by Duedall and Weyl (1967), by Duedall (1972), by Ward and Millero (1975) and by Poisson and Chanu (1976). Earlier values for these quantities were taken from measurements in NaCl solutions (Owen and Brinkley, 1941) or were estimated from data for single salt solutions on the assumption that the partial molal volume of a salt in solutions of electrolytes depends only on the ionic strength of the solution (Wirth, 1940; Owen and Brinkley, 1941). Owen and Brinkley also derived estimates of the partial molal compressibilities of salts in "salt water" (0.725 m NaCl) at atmospheric pressure from those in water by making use of Tamann's (1907) hypothesis of the effective pressure due to an ionized solute. More recently, Millero *et al.* (1977) experimentally determined the partial molal volumes of a large number of electrolytes in 0.725 m NaCl solution at 25°C; Millero (1970) presents results which give the temperature dependence of the partial molal volume of sodium chloride in its own solution at this concentration. Millero *et al.* (1974) give data from which the partial molal compressibility of sodium chloride in 0.725 m NaCl can be calculated at several temperatures; Allam and Lee (1966) present similar data for sodium chloride at 25°C. Chen *et al.* (1977) measured the apparent molal volumes of several salts in binary aqueous solutions from 0 to 1000 bars at several temperatures; their results for NaCl can be used to calculate the partial molal compressibility of this salt in 0.725 m solutions. Millero (1982a) calculated values for the isothermal partial molal compressibility at atmospheric pressure for most of the ions in seawater from results for the adiabatic partial molal compressibility in 0.725 m NaCl (Millero *et al.*, 1980b) and from the estimated values for the partial molal compressibility changes for the ionization of boric acid and bicarbonate ion in seawater (Millero, 1979).

In this paper we present results for the effect of pressure on the partial equivalent volumes of salts of the major ions in 35‰ seawater at 10 and 25°C for increments of 400 and 1000 bars and derive estimates of their partial equivalent compressibilities at atmospheric pressure.

2. Method

a. Theory. The effect of pressure on the partial equivalent volumes of the salts investigated was derived from measurements of the variation of the compression of solutions of seawater and added salt with the concentration of the latter. If the addition of n equivalents of a salt to a volume V_{sw} (cm³) of seawater results in a solution volume V , then the apparent equivalent volume ϕ_v of the salt in seawater is defined here by

$$\phi_v = (V - V_{sw})/n . \quad (4)$$

From this definition, if r is the mass ratio of the added salt to seawater sample, then the apparent equivalent volume (cm³/equivalent) of the salt in seawater at applied pressure P is given by

$$\phi_v(P) = \phi_v(0) \frac{V(P)}{V(0)} + \frac{M}{\rho^\circ(0)} \frac{\left(\frac{V(P)}{V(0)} - \frac{V^\circ(P)}{V^\circ(0)} \right)}{r} \quad (5)$$

where $V(P)$ is the volume of the solution at applied pressure P , M is the equivalent weight (grams) of the salt, $\rho(0)$ is the density (g/cm³) at atmospheric pressure, and the superscript $^\circ$ denotes the seawater sample. In the limit as $r \rightarrow 0$ equation 5 gives for the partial equivalent volume (cm³/equivalent),

$$\bar{V}(P) = \bar{V}(0) \frac{V^\circ(P)}{V^\circ(0)} + \frac{M}{\rho^\circ(0)} \lim_{r \rightarrow 0} \frac{\left(\frac{V(P)}{V(0)} - \frac{V^\circ(P)}{V^\circ(0)} \right)}{r} . \quad (6)$$

The effect of pressure on the partial equivalent volume is thus

$$\Delta \bar{V}(P) = \bar{V}(P) - \bar{V}(0) = -\bar{V}(0)C^\circ(P) - \frac{M}{\rho^\circ(0)} \lim_{r \rightarrow 0} \frac{\Delta^r C(P)}{r} , \quad (7)$$

where $C(P) = 1 - \frac{V(P)}{V(0)}$ is the compression and $\Delta^r C(P) = C^r(P) - C^\circ(P)$.

b. Experimental procedure. The salts investigated were NaCl, KCl, Na₂SO₄, MgSO₄ · 7H₂O, Ca(NO₃)₂ · 4H₂O and NaNO₃ and were Fisher certified reagents. They were treated in the manner described by Duedall and Weyl (1967) before weighing. In the case of the hydrated salts both the mass of the salt and the mass of the seawater sample were corrected for the water of hydration before computing r ; the salinity of the original seawater sample was also corrected for this added water. The seawater source was Batch No. P57 I.A.P.S.O. Standard Seawater. KHCO₃ was also studied, but, in this case, the greatest value of r attainable without precipitation (of presumably CaCO₃) during a run was too small ($r \leq 0.002$) to give results for $\Delta V(P)$ with a standard error precision better than 0.5 cm³/equivalent; for this reason they are not reported here.

The volume compressions were measured in a fused quartz dilatometer using the apparatus and procedure for the measurement of the compression of seawater described previously by Bradshaw and Schleicher (1976). In the latter work two Aminco dead weight piston gages of identical piston-cylinder design were used: gage 1 was used for the main body of volume observations (Table 1A of that work), on which the seawater compression formula which was presented there was based; gage 2 was used for two abbreviated runs (in Table 1B of the same work) on 34.897‰ salinity seawater at 10 and 25°C (on The International Practical Temperature Scale of 1948, IPTS-48). The two abbreviated runs referred to provide the reference seawater data ($r = 0$) for the rest of the work reported here, which, with the exception of the NaCl runs, was also done using gage 2. Gage 1 was used for the NaCl runs, but comparisons of the compression results on 35‰ salinity seawater at 10°C (see data in Tables 1A and 1B of the previous work) show that within the precision of the compression measurements [standard error for a single observation = 2×10^{-6} (Bradshaw and Schleicher, 1976)] the two gages gave the same results.

In the work at $r > 0$, $V(P)$ at 10 and 25°C (IPTS 48) were measured at the applied pressures of the above abbreviated seawater runs, i.e., at approximately 0.5 (sometimes), 6, 10, 17, 400, 1000 and 6 bars, in the order given. The $P \approx 0.5$ bar points were not used in the treatment of the data because of the possible presence of a gas phase in the sample volume at that pressure (see Bradshaw and Schleicher, 1976); the final 6 bar points were used only in making an estimate of precision for the 25°C compressions (see below). Measurements were made first at 10°C and then, with the exception of a single temperature NaCl run ($r = 0.011070$), continued at 25°C using the same sample.

Temperature deviations from the nominal temperatures of the runs did not exceed 0.004°C with one exception (0.007°C) and the volumes were calculated at these temperatures using thermal expansion coefficients for seawater in the work-up of the data.

c. Analysis of measurements. $V(0)$, which is needed to compute compressions, was found by linear least-squares extrapolation of the three low pressure points (excluding $P \approx 0.5$ bars). Such extrapolation made on the volume—pressure results in Table 1A of the previous work, where there were more points evenly distributed throughout the pressure range, agreed to within 1.5 ppm of the volume with those obtained by “best” least-squares polynomial fits to the entire set of data for $P \geq 6$ bars. Also, the linearity of the points at 6, 10 and 17 bars (< 0.8 ppm of the volume) was well within the precision of the measurements.

The changes in solution compression ($\Delta^r C(P)$) with r are given in Table 1 for applied pressures of 400.1 and 999.5 bars at 10 and 25°C. They were computed by first adjusting the seawater compressions at 400.1 and 999.5 bars and 34.897‰

Table 1. Observed changes in solution compression [$\Delta^r C(P)$] as a function of r , the mass ratio of added salt to seawater sample. S = salinity (‰) of the sample; T = temperature (IPTS-48); and P = applied pressure (bars).

Salt	S_1	r_1	$\Delta^{r_1} C(P) \times 10^9$			
			$T = 10^\circ\text{C}$		$T = 25^\circ\text{C}$	
			$P = 400.1$	$P = 999.5$	$P = 400.1$	$P = 999.5$
NaCl	35.000	0.002398	- 81.3	-177.4	- 65.0	-149.8
KCl	34.896	0.003963	-102.3	-218.9	- 82.6	-184.2
Na ₂ SO ₄	34.900	0.003692	-138.9	-307.0	-112.5	-260.5
NaNO ₃	34.910	0.003831	- 85.6	-191.4	- 59.0	-142.0
Ca(NO ₃) ₂	34.880	0.003375	- 65.0	-148.2	- 41.7	-103.4
MgSO ₄	34.900	0.003470	-138.8	-311.2	-117.4	-266.4

Salt	S_2	r_2	$\Delta^{r_2} C(P) \times 10^9$			
			$T = 10^\circ\text{C}$		$T = 25^\circ\text{C}$	
			$P = 400.1$	$P = 999.5$	$P = 400.1$	$P = 999.5$
NaCl	34.934	0.005549	-188.3	-410.2	-153.6	-342.8
KCl	34.900	0.010870	-270.2	-584.8	-221.4	-491.4
Na ₂ SO ₄	34.895	0.008580	-315.8	-704.2	-265.6	-596.7
NaNO ₃	34.891	0.009662	-214.5	-478.2	-162.7	-372.8
Ca(NO ₃) ₂	34.912	0.008230	-158.2	-354.7	-120.7	-275.0
MgSO ₄	34.900	0.007873	-310.5	-695.3	-266.0	-604.7

Salt	S_3	r_3	$\Delta^{r_3} C(P) \times 10^9$			
			$T = 10^\circ\text{C}$		$T = 25^\circ\text{C}$	
			$P = 400.1$	$P = 999.5$	$P = 400.1$	$P = 999.5$
NaCl	34.921	0.011070	-376.2	-818.2		

salinity to the pressures and salinities of the seawater samples in the runs for $r > 0$. The adjustments were made using the equation of state for seawater given in Bradshaw and Schleicher (1976). The pressure differences did not exceed 0.1 bar and the maximum salinity difference was 0.103‰ (Table 1).

The standard error of $\Delta^r C(P)$ is that of the difference in two independent observations of compression. At 10°C this is found, using 2×10^{-6} for the standard error of a single observation of compression (see above), to be $\sqrt{2} \times 2 \times 10^{-6}$ at all pressures. The measurements at 25°C differed from those at 10°C in that the dilatometer capillary bore had been wetted with the distilled water used as the pressure transmitting fluid during the previous run at 10°C. The standard error in this case was estimated in the following manner. At 1000 bars its value of 4.7×10^{-6} was calculated from the standard deviation of the differences between the initial and final 10°C volume measurements at 6 bars, using all of the results from the present and from the previous work, and at 400 bars its value of 3.2×10^{-6} was estimated

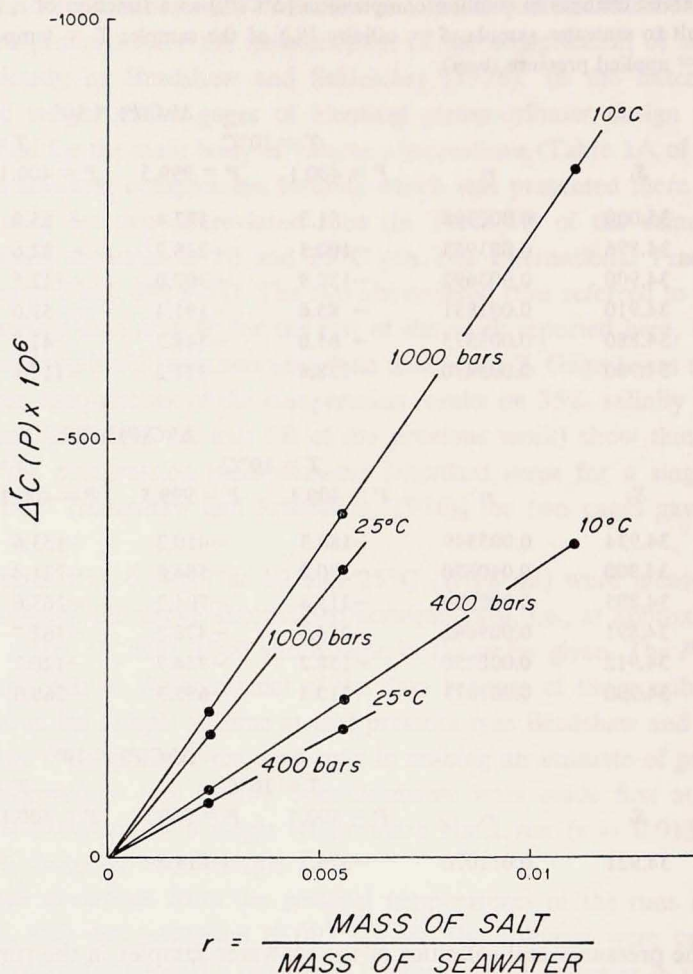


Figure 1. Change in compression ($\Delta^r C(P)$) of solutions of sodium chloride in seawater with the mass ratio (r) of salt added to original seawater sample.

by assuming that the standard error associated solely with the wetting of the capillary bore varied linearly from 0 at 6 bars to $[(4.7)^2 - (2\sqrt{2})^2]^{\frac{1}{2}} \times 10^{-6}$ at 1000 bars.

The results for $\Delta^r C(P)$ vs. r for NaCl are plotted in Figure 1, where the least-squares linear fit through the origin has also been drawn. Linear fits were also made to the results for the other salts. The linearity of the points in each case can be judged using the rms deviations about the straight lines which are given in Table 2.

In general, the compression of an aqueous salt solution at a fixed pressure not only decreases with increasing salt concentration, but does so at a decreasing rate [see, e.g., Gibson (1933, 1934)]. Thus, curves of $\Delta^r C(P)$ vs. r in the present case

Table 2. RMS deviations about straight line least-squares fit through the origin for $\Delta^r C(P)$ vs. r data.

Salt	$10^0 \times$ RMS deviation			
	10°C		25°C	
	$P = 400$ b	$P = 1000$ b	$P = 400$ b	$P = 1000$ b
NaCl	0.0	0.1	0.9	1.1
KCl	2.5	3.8	1.3	3.4
Na ₂ SO ₄	2.0	2.6	1.2	2.4
NaNO ₃	0.4	1.2	3.6	3.8
Ca(NO ₃) ₂	0.1	1.8	5.1	6.1
MgSO ₄	1.3	3.1	0.1	0.1

should be concave upward (concave downward as presented in Fig. 1). If the curves are linear to a sufficient precision over the range of r , then the quantity $\lim_{r \rightarrow 0} \frac{\Delta^r C(P)}{r}$

in Eq. 7 can be found by taking the weighted average of the $\Delta^r C(P)/r_i$ using $w_i = r_i^2/\sigma^2$ as the weight, where σ is the standard error of $\Delta^r C(P)$ that was estimated above; more simply, this limit is equal to the slope of a linear fit of the type shown in Figure 1. If the curves are not linear over the range of r , the above method gives a biased estimate of the limit; a less biased estimate can be obtained by linearly extrapolating $\Delta^r C(P)/r_i$ to $r = 0$. Application of the latter method to curves that are actually linear results in a loss of precision compared with the method of weighted averages, however, and, also in cases where nonlinearity of the curves exists but is small, the reduction in bias error may be exceeded by the loss in precision of the estimate.

Some time before this paper was written preliminary results for the effect of pressure on partial equivalent volumes in seawater, computed by the method of weighted averages, were communicated to F. J. Millero; partial molal compressibilities at 25°C and atmospheric pressure derived from these results were compared by Millero (1982a) with those in 0.725 m NaCl solution which he had calculated from adiabatic partial molal compressibilities based on sound speed measurements (Millero *et al.*, 1980b). The agreement between the two sets of results was nearly within the combined experimental error. The final results presented here for the effect of pressure on partial equivalent volumes, however, have been computed by the method of extrapolation, because there seems to be no independently valid reason for doing otherwise; but, for comparison, the differences in the effect of pressure on the partial equivalent volumes calculated by the two methods, as well as the corresponding differences in partial equivalent compressibilities, are also presented below.

The extrapolations in the case of the NaCl results at 400 and 1000 bars at 10°C required weighted least-squares fits; in all other cases a straight line was simply

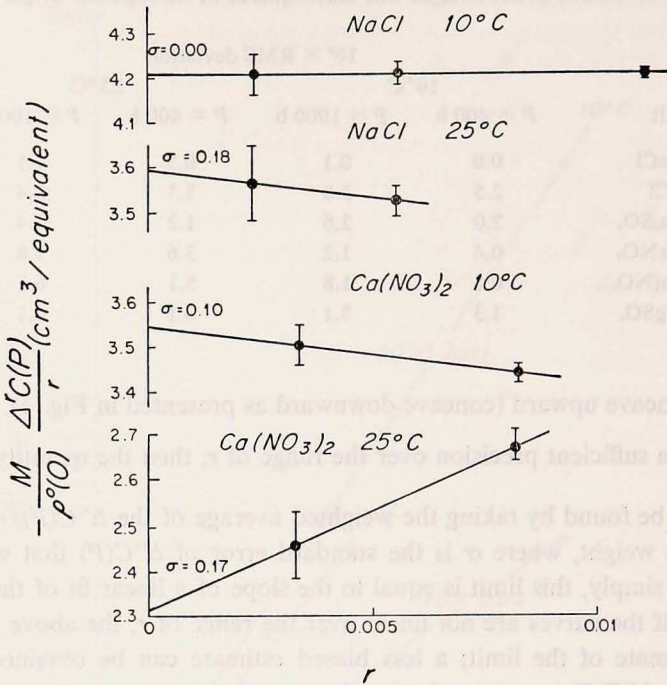


Figure 2. Examples of extrapolations of $-\frac{M}{\rho^{\circ}(0)} \frac{\Delta C(P)}{r}$ to its value at $r = 0$ (see Eq. 7). Pressure equals 1000 bars. The standard error bar is shown for each point.

drawn through the two points. The standard error of the intercept at $r = 0$ was calculated using $1/W_i$ for the variances of $\Delta^r C(P)/r_i$. Examples of the extrapolations are illustrated in Figure 2. To complete the calculation of $\Delta \bar{V}(P)$ by Eq. 7, Duedall and Weyl's (1967) Eq. 2 for the partial equivalent volume at atmospheric pressure, $\bar{V}(0)$, was used.

Both the method of extrapolation and the method of weighted averages were tested for the case of "seasalt" at 10°C on seawater equation of state results. The Bradshaw and Schleicher (1976) compression formula and the new UNESCO equation of state (Millero *et al.*, 1980a) were used. Compressions from both of these equations exhibit the characteristics for salt solutions described above. From the equations, exact values of \bar{V}_{seasalt} at $S = 30.709\%$ and applied pressures of 400.14 and 999.53 bars were calculated, and values of $V(P)/V(0)$ at the same pressures and salinities of 30.709, 34.891 and 38.878 were generated. These salinities, which are on the new Practical Salinity Scale 1978 (Lewis, 1980), correspond to the salinities in Table 1A of the Bradshaw and Schleicher paper. Observed values of

Table 3. Comparison of exact and extrapolated values for the effect of pressure on the partial equivalent volume of "seasalt" in 30.709‰ salinity seawater at 10°C IPTS-48 (9.9957°C IPTS-68).

P(applied, bars)	$\Delta\bar{V}_{s,s}(P)$ (cm ³ /equivalent)				
	Exact	B&S Compressions		UNESCO EOS Compressions	
		Formula	Observed	Exact	Formula
400.14	1.84	1.84	1.94	1.78	1.78
999.53	3.99	4.01	3.99	3.87	3.87

$V(P)/V(0)$ at the above salinities and pressures (after small adjustments in $V(P)$, if necessary) were also calculated from the same table. r was calculated from the weight dilution salinity S of the Practical Salinity Scale using

$$r = 10^{-3} (S - 30.709) / (1 - 10^{-3} S) \quad (8)$$

Exact values for \bar{V}_{seasalt} were calculated from the relation

$$\bar{V}_s(P) = M_s \bar{v}_s(P) = M_s \left[v^\circ(P) + \left(1 - \frac{S}{1000} \right) \frac{\partial v^\circ(P)}{\partial S} \cdot 1000 \right], \quad (9)$$

where M_s is the equivalent weight of the salt and $\bar{v}_s(P)$ and $v^\circ(P)$ are the partial specific volume of "seasalt" and the specific volume of seawater at pressure P . For "seasalt" the value 57.7977 g, computed for the artificial seawater of Kester *et al.* (1967), was taken as the equivalent weight.

The results for the method of extrapolation are shown in Table 3. Extrapolations to $r = 0$ using the UNESCO formula agree to within 0.01 cm³/equivalent with the exactly calculated values for the effect of pressure on the partial equivalent volume, while those from the Bradshaw and Schleicher (B&S) formula differ by not more than 0.02 cm³/equivalent. The extrapolations from the observed values of the compressions reflect the random errors in these unsmoothed values. On this basis, the accuracy of the method appears to be better than 0.02 cm³/equivalent for the values of r used ($r_1 \approx 0.0043$ and $r_2 \approx 0.0085$) in the case of "seasalt," and it should certainly be a good estimate in the case of NaCl, the principal component of "seasalt."

In comparison, calculation of $\lim_{r \rightarrow 0} \frac{\Delta r C(P)}{r}$ by the method of weighted averages gives results for the pressure effect on the partial equivalent volume of "seasalt" that are too low by 0.10 and 0.21 cm³/equivalent at 400 and 1000 bars in the case of the B&S equation and by slightly less than one-half of these amounts in the case of the UNESCO equation. The disagreements in the errors in the two cases reflect the slight differences in curvature of the compressions as a function of r given by the two equations.

Table 4. Change in partial equivalent volume of various salts in seawater with applied pressure (calculated by the method of extrapolation—see text). \bar{V}_s = partial equivalent volume ($\text{cm}^3/\text{equivalent}$); P = applied pressure in bars; T = temperature (IPTS-48); and $\sigma_{\Delta\bar{V}_s}$ = standard error; salinity = 35‰.

Salt	$\Delta\bar{V}_s(P)$ ($\sigma_{\Delta\bar{V}_s}$)			
	$T = 10^\circ\text{C}$		$T = 25^\circ\text{C}$	
	$P = 400.1$	$P = 999.5$	$P = 400.1$	$P = 999.5$
NaCl	1.64(0.00)	3.54(0.00)	1.22(0.12)	2.83(0.18)
KCl	1.45(0.08)	3.00(0.08)	1.07(0.09)	2.36(0.13)
Na_2SO_4	2.64(0.09)	5.47(0.09)	1.92(0.10)	4.56(0.15)
NaNO_3	1.40(0.09)	3.10(0.09)	0.71(0.10)	1.87(0.15)
$\text{Ca}(\text{NO}_3)_2$	1.20(0.10)	2.76(0.10)	0.50(0.11)	1.47(0.17)
MgSO_4	2.37(0.08)	5.31(0.08)	1.97(0.09)	4.46(0.13)

3. Results

The calculated changes in partial equivalent volumes with pressure (by the method of extrapolation) are given in Table 4. The standard error of these values is given in parentheses; it was taken equal to the standard error of the intercept for each extrapolation. The differences between these values and those calculated by the method of weighted averages are shown in Table 5.

The partial equivalent compressibility is defined here by $\bar{\kappa}_s = -\frac{\partial\bar{V}_s}{\partial P}$. Values for this quantity at atmospheric pressure and their standard errors were calculated from quadratic fits to the data in Table 4. The results are given in Table 6. The differences in partial equivalent compressibilities which correspond to the differences in the effect of pressure on partial equivalent volumes computed by the method of extrapolation and by the method of weighted averages (Table 5) are shown in Table 7.

Table 5. Comparison of changes in partial equivalent volume with applied pressure calculated by the method of weighted averages (WA) with those calculated by the method of extrapolation (E) (see Table 4). \bar{V}_s = partial equivalent volume ($\text{cm}^3/\text{equivalent}$); P = applied pressure (bars); and T = temperature (IPTS-48); salinity = 35‰.

Salt	$[\Delta\bar{V}_s(P)]_{\text{WA}} - [\Delta\bar{V}_s(P)]_{\text{E}}$			
	$T = 10^\circ\text{C}$		$T = 25^\circ\text{C}$	
	$P = 400.1$	$P = 999.5$	$P = 400.1$	$P = 999.5$
NaCl	0.00	0.00	0.06	0.01
KCl	-0.10	-0.15	-0.05	-0.13
Na_2SO_4	-0.23	-0.12	0.06	-0.11
NaNO_3	-0.02	-0.06	0.19	0.20
$\text{Ca}(\text{NO}_3)_2$	-0.01	-0.10	0.29	0.34
MgSO_4	-0.06	-0.13	0.00	0.00

Table 6. Partial equivalent compressibilities ($\bar{\kappa}_s$) of various salts in seawater at atmospheric pressure. $\bar{\kappa}_s = -\frac{\partial \bar{V}_s}{\partial P}$ in $\text{cm}^3/\text{equivalent}/\text{bar}$; T = temperature (IPTS-48); salinity = 35‰; and $\sigma_{\bar{\kappa}_s}$ = standard error.

Salt	$10^4 \times \bar{\kappa}_s (10^4 \times \sigma_{\bar{\kappa}_s})$	
	$T = 10^\circ\text{C}$	$T = 25^\circ\text{C}$
NaCl	-44.7(0.0)	-32(5)
KCl	-40(3)	-29(4)
Na_2SO_4	-73(4)	-50(4)
NaNO_3	-38(4)	-17(4)
$\text{Ca}(\text{NO}_3)_2$	-32(4)	-11(5)
MgSO_4	-63(3)	-52(4)

Duedall and Weyl (1967) calculated the partial equivalent volume of "seasalt," \bar{V}_{ss} , from the expression

$$\bar{V}_{ss} = \bar{V}_{\text{NaCl}} + \sum_i X_i \bar{V}_{\Delta i}, \quad (10)$$

where X_i is the fraction of the equivalents contributed by ion i in seawater and $\bar{V}_{\Delta i}$ is the partial equivalent volume of that ion minus that of Na^+ in the case of cations or of Cl^- in the case of anions. The change in \bar{V}_{ss} with pressure $\Delta \bar{V}_{ss}(P)$ can thus be calculated from

$$\Delta \bar{V}_{ss}(P) = \Delta \bar{V}_{\text{NaCl}}(P) + \sum_i X_i \Delta \bar{V}_{\Delta i}(P). \quad (11)$$

The calculation is similar to that for \bar{V}_{ss} in Table 4 of Duedall and Weyl, except that the bicarbonate ion is not included. This exclusion has an insignificant effect on

Table 7. Comparison of partial equivalent compressibilities ($\bar{\kappa}_s$) derived from values for the effect of pressure on partial equivalent volumes computed by two methods (see text), the method of extrapolation (E) and the method of weighted averages (WA). $\bar{\kappa}_s = -\frac{\partial \bar{V}_s}{\partial P}$ in $\text{cm}^3/\text{equivalent}/\text{bar}$; T = temperature (IPTS-48); and salinity = 35‰.

Salt	$10^4 \times [(\bar{\kappa}_s)_{\text{WA}} - (\bar{\kappa}_s)_{\text{E}}]$	
	$T = 10^\circ\text{C}$	$T = 25^\circ\text{C}$
NaCl	0	-2
KCl	3	1
Na_2SO_4	8	-3
NaNO_3	1	-7
$\text{Ca}(\text{NO}_3)_2$	0	-10
MgSO_4	1	0

Table 8. Comparison of results for effect of pressure on the partial equivalent volume ($\text{cm}^3/\text{equivalent}$) of "seasalt" at $S = 35\%$.

$P(\text{bars})$	$\Delta\bar{V}_{ss}(P)$					
	Equation of State (EOS)		Equation 11 (E11)		$\delta(\text{E11} - \text{EOS})$	
	10°C	25°C	10°C	25°C	10°C	25°C
400.1	1.73	1.42	1.68	1.28	-0.05	-0.14
999.5	3.75	3.08	3.67	2.95	-0.08	-0.13

the results because of the relatively small concentration of HCO_3^- . $\Delta\bar{V}_{\text{NaCl}}(P)$ and $\Delta\bar{V}_{\Delta_i}(P)$ were obtained at each pressure from the results in Table 4 of the present paper; X_i were calculated from the composition of the artificial seawater of Kester *et al.* (1967).

A comparison of the above results for $\Delta\bar{V}_{ss}(P)$ with those calculated from the B&S equation of state is shown in Table 8. Values for $\Delta\bar{V}_{ss}(P)$ from the UNESCO equation of state differ by at most $0.02 \text{ cm}^3/\text{equivalent}$ at $S = 35\%$ from those of the B&S equation and are not shown. The standard errors of the $\Delta\bar{V}_{ss}(P)$ computed from Eq. 11 can be estimated from the standard errors of the components: they are $0.02 \text{ cm}^3/\text{equivalent}$ for both pressures at 10°C and 0.11 and $0.16 \text{ cm}^3/\text{equivalent}$ at 400 and 1000 bars, respectively, at 25°C . At both temperatures the $\Delta\bar{V}_{ss}(P)$ which are calculated from the $\Delta\bar{V}_s(P)$ of the component salts underestimate those obtained from the equation of state. The major sources of these differences are errors in the equation of state which affect the saline contraction coefficient at higher pressures (see Eq. 9, where an error of $.1 \text{ cm}^3/\text{equivalent}$ in $\bar{V}_s(P)$ corresponds to an error of $1.7 \times 10^{-6} \text{ cm}^3/\text{g}/\%$ salinity in $\frac{\partial v^\circ(P)}{\partial S}$) and errors in the present results for NaCl, the principal component of "seasalt."

The partial equivalent compressibility of "seasalt" was also estimated using values for its component salts given in Table 6. The method was the same as that used in estimating the partial equivalent volume of "seasalt" from its components. The results and their standard errors are compared in Table 9 with those calculated from the B&S equation of state using

Table 9. Comparison of results for partial equivalent compressibilities of "seasalt" ($\bar{\kappa}_{ss}$, $\text{cm}^3/\text{equivalent}/\text{bar}$) at salinity = 35% and one atmosphere. $\sigma_{\bar{\kappa}_{ss}}$ = standard error.

$\bar{\kappa}_{ss} \times 10^4 (\sigma_{\bar{\kappa}_{ss}} \times 10^4)$			
Equation of state		(Table 6)	
10°C	25°C	10°C	25°C
-48	-39	-45(1)	-34(5)

Table 10. Comparison of partial equivalent compressibilities ($\bar{\kappa}_s$) in 35‰ salinity seawater at one atmosphere and 25°C from this work with those of others in 0.725 m NaCl solution. $\sigma_{\bar{\kappa}_s}$ = standard error.

Salt	10 ⁴ $\bar{\kappa}_s$ (10 ⁴ $\sigma_{\bar{\kappa}_s}$)		
	This work		Others
NaCl	-32(5)	-37 ^α	-45 ^β , -36 ^γ , -36 ^δ , -39 ^ε
KCl	-29(4)	-31 ^α	-39 ^β
Na ₂ SO ₄	-50(4)	-53 ^α	-67 ^β
NaNO ₃	-17(4)	-25 ^α	-31 ^β
Ca(NO ₃) ₂	-11(5)	-25 ^α	-25 ^β
MgSO ₄	-52(4)	-55 ^α	-66 ^β

^α Millero (1982a)

^β Owen and Brinkley (1941)

^γ Chen *et al.* (1977)

^δ Millero *et al.* (1974)

^ε Allam and Lee (1966)

$$\frac{\partial \bar{V}_s(P)}{\partial P} = M_s \left[\frac{\partial v^\circ(P)}{\partial P} + \left(1 - \frac{S}{1000} \right) \frac{\partial}{\partial P} \left(\frac{\partial v^\circ(P)}{\partial S} \right) \cdot 1000 \right] \quad (12)$$

which is the derivative of Eq. 9 with respect to pressure.

Quadratic fits to the equation of state results for $\Delta \bar{V}_{ss}(P)$ versus applied pressure in Table 8 yield values for $\bar{\kappa}_{ss}$ at atmospheric pressure of -47×10^{-4} and -38×10^{-4} cm³/equivalent/bar at 10° and 25°C. The good agreement with the exactly derived values gives weight to the use of quadratic fits in obtaining partial equivalent compressibilities at atmospheric pressure.

4. Comparisons

Values for the partial molal compressibility of the salts investigated here in 0.725 m NaCl solution at 25°C and atmospheric pressure were recently calculated by Millero (1982a) from experimental adiabatic partial molal compressibilities. His values and Owen and Brinkley's estimates of the same quantities have been converted to partial equivalent compressibilities, and these are compared with the present values for these salts in Table 10. Also shown there are (1) values for the partial equivalent compressibility of NaCl in 0.725 m NaCl solution derived from the empirical formula of Chen *et al.* (1977) for the apparent molal volume of this salt in water as a function of molality, pressure and temperature and (2) values for the same quantity calculated from the apparent molal compressibility $\left(\phi_{\kappa} = -\frac{\partial \phi_V}{\partial P} \right)$ results of Allam and Lee (1966) and of Millero *et al.* (1974; their Eq. 10); in both cases, the calculation used the relation

$$\bar{\kappa}_s(P) = -\frac{\partial \bar{V}_s(P)}{\partial P} = -\frac{\partial \phi_V(P)}{\partial P} - m \frac{\partial}{\partial m} \left(\frac{\partial \phi_V(P)}{\partial P} \right) \quad (13)$$

which is derived from the definition of apparent molal volume.

All of our results for the partial equivalent compressibility in seawater at 25°C and one atmosphere are lower in absolute value than those for the same salts in 0.725 m NaCl; this is consistent with the formation of ion pairs in seawater (Millero, 1982b).

Owen and Brinkley's theoretical estimates are the highest in absolute value of all the results in Table 10. The latter investigators estimated their values using Tamann's hypothesis that the water in aqueous solutions of ionized solutes, such as NaCl, is subject to an "effective pressure" due to the solute, in addition to the external pressure; on this basis they found that the partial molal compressibility at infinite dilution of an electrolyte in 0.725 m NaCl solution should be approximately 0.87 times the corresponding quantity in water. Of the salts studied here, determinations of the partial molal compressibilities at infinite dilution in water of NaCl and KCl from sound speed measurements in dilute solution (Garnsey *et al.*, 1969; Owen and Kronick, 1961) indicate that the values that Owen and Brinkley used for these quantities are too large in absolute value. Multiplying the above, more recent values by 0.87 give -40 and -35 for $\bar{\kappa}_s \times 10^4$ of NaCl and KCl in 0.725 m NaCl solution at 25°C; these calculations bring all of the values for these salts in 0.725 m NaCl solution into closer agreement and reduce the differences between our values in seawater and those estimated by Owen and Brinkley's method by about one-half.

The differences at 25°C between our values for the partial equivalent compressibility in seawater and those of Millero (1982a) in 0.725 m NaCl solution are largest for NaNO₃ and Ca(NO₃)₂. In both of these cases, but especially in the case of Ca(NO₃)₂, not only are the compression differences, $\Delta^r C(P)$, more nonlinear than average with r_i at both pressures (see Table 2), but they decrease with r at an increasing rate, that is to say $-\Delta^r C(P)/r$ increases with r (see Fig. 2 for the case of Ca(NO₃)₂ at 25°C and 1000 bars); referring to the earlier discussion of the expected curvature of $\Delta^r C(P)$ vs. r , this probably indicates a larger than average experimental error. The sign of the error would be such that the effect of pressure on the partial equivalent volume would be underestimated, and, consequently, so would the absolute value of the partial equivalent compressibility. Comparison of the differences in Table 7 between the partial equivalent compressibilities for these salts computed by the method of weighted averages and by the method of extrapolation at 10°C with those at 25°C also suggests the existence of such an error.

At 10°C our results for the partial equivalent compressibility of NaCl in seawater (Table 6) agree well with those of Millero *et al.*, 1974 ($10^4 \bar{\kappa}_s = -45$); and Chen *et al.*, 1977 ($10^4 \bar{\kappa}_s = -47$).

In summary, where comparisons are possible, our results for the partial equivalent

compressibility of salts in seawater at one atmosphere are systematically lower in absolute value than the *experimentally* determined values of others in 0.725 m NaCl solution, as expected, but, with the exception of NaNO_3 and $\text{Ca}(\text{NO}_3)_2$ at 25°C , they are still in fair to good agreement with these. In the case of the two exceptions, the larger differences appear to be due to larger experimental errors. For these cases a better estimate of the partial equivalent compressibility is probably that obtained using the assumption that the change in compression with concentration of added salt is linear: this is because this assumption gives results in the remaining cases which are generally in good agreement with those calculated not using the assumption. The results for $10^4 \times \bar{\kappa}_s$ would then be (using Tables 6 and 7) -24 and -21 for NaNO_3 and $\text{Ca}(\text{NO}_3)_2$.

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