umes, $\sigma(V^E)$, are given in Table II.

It is observed that the V^E values for the binary mixtures of tetrahydrofuran with chloroform, carbon tetrachloride, acetonitrile, and acetone are negative over the entire composition range. For mixtures containing 1,2-dichloroethane, chloroform, and carbon tetrachloride, V^E at equimolar concentration decreases linearly with the number of chlorine atoms in the molecule. These observations support the view of Bolinga et al. (*10*) that the specific interactions of the type $-\mathrm{Cl}\cdots\mathrm{O}<$, $-\mathrm{C}{\equiv}\mathrm{N}\cdots\mathrm{O}<$, and $>\mathrm{C}{=}\mathrm{O}\cdots\mathrm{O}<$ may be responsible for negative excess volumes. Mixtures of tetrahydrofuran with methyl formate, ethyl acetate, and nitromethane have been found to exhibit positive V^E. The data do not indicate any obvious relationship between V^E and the electron donor-acceptor abilities of the solution constituents. Simultaneous thermodynamic and structural investigations on these solutions might yield some qualitative insight to distinguish the contributions to thermodynamic behavior of liquid solutions due to specific and nonspecific interactions. Further investigations on these mixtures are under way.

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Equations of State for NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ Aqueous Solutions at High Pressures

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Equations of state for NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ aqueous solutions have been determined from the sound speeds over the ranges of I = 0–1 m, 0–40 °C, and 0–1000 bar with a precision estimated to be better than 30 × 10^{-6} $cm^3\ g^{-1}$ in specific volume. The results agree reasonably well with the data of various direct measurements.

Introduction

Few measurements have been made on the high-pressure *PVT* properties of NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$, aqueous solutions. Probably the most extensive and precise data given to date are the direct specific volume measurements of Emmet (*1*) and Chen, Emmet, and Millero (*2*). The direct specific volumes were measured on a high-precision magnetic float densimeter (*1*, *3*, *4*). In this study, we will take a different approach and determine the *PVT* properties from the sound-speed data (*5*) and the 1-atm density equations obtained in a recent article (*6*). The results will be compared with the data of various direct measurements.

Equation of State from Sound Speeds

The method used to determine an equation of state from sound speed has been described in detail elsewhere (*7*, *8*). The equation of state is in the form

$$K^P = v^0P/(v^0 - v^P) = K^0 + AP + BP^2 \qquad (1)$$

where K^P and K^0 are the secant bulk moduli at applied pressures P and 0 (1 atm), respectively, v^P and v^0 are respectively the specific volumes of the solutions at applied pressures P and 0, and A and B are temperature- and concentration-dependent parameters. Specific volumes are used in preference to densities because we have found that significantly simpler equations can be used to represent volume data at high pressures.

The specific volumes of the aqueous solutions at 1 atm are represented by eq 2 (*6*), where $v^0 = 1/d_0$ is the specific

$$1/v^0 = d_0 + am + bm^{3/2} + cm^2 + dm^{5/2} \qquad (2)$$

volume of pure water at 1 atm, m is the concentration in molality, and a, b, c, and d are temperature-dependent parameters. The constants for eq 2 are given in a previous paper (*6*).

The 1-atm sound speeds in the NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ aqueous solutions (*5*) are combined with the 1-atm specific volumes and heat capacities (*7*, *9*–*11*) to determine K^0 following the procedures described elsewhere (*7*, *8*). Values of K^0 are fit into the following equation

$$K^0 - K_0{}^0 = em + fm^{3/2} + gm^2 \qquad (3)$$

where e, f, and g are temperature-dependent parameters given in Table I, and $K_0{}^0$ is the secant bulk modulus of pure water at 1 atm (*12*, *13*).

$$K_0{}^0 = 19652.17 + 148.183t - 2.29995t^2 + 0.012810t^3 - 4.91564 \times 10^{-5}t^4 + 1.03553 \times 10^{-7}t^5 \qquad (4)$$

It should be noted that eq 3 reduces to $K^0 = K_0{}^0$ when the concentration of the salt, m, reduces to zero. This makes the equation for the salts consistent with the pure-water equation

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Table I. Coefficients for Eq 3

	variables	NaCl	$MgCl_2$	Na_2SO_4	$MgSO_4$
e	m	3225.04	5444.84	8951.89	7443.28
	mt	−31.46	−27.33	−75.54	−48.56
	mt^2	0.3061	0.8552	1.0637	1.413
	mt^3	1.58E-4	−0.0259	−5.04E-3	−0.0184
	mt^4		3.589E-4		
f	$m^{3/2}$	−205.27	−456.27	−2752.99	−2343.01
	$m^{3/2}t$	5.369	−1.7539	45.49	22.76
	$m^{3/2}t^2$	−0.0883	−0.06032	−0.5858	−0.3168
g	m^2	28.26	463.75	1708.93	1981.43
	m^2t	−0.431	−2.449	−11.43	−12.75
validity range		0–55 °C, I = 0–1.0 *m*	0–50 °C, I = 0–1.2 *m*	0–50 °C, I = 0–1.0 *m*	0–50 °C, I = 0–2.0 *m*
$10^6\sigma$, bar^{-1}		0.006	0.007	0.003	0.027

Table II. Coefficients for Eq 5 and 6

	variables	NaCl	$MgCl_2$	Na_2SO_4	$MgSO_4$
h	mP	0.2567	0.4407	1.1153	1.1939
	mtP	−6.88E-3	−0.0142	−0.01896	−1.054E-3
	mt^2P	1.22E-4	2.10E-4	5.18E-5	−2.00E-4
i	$m^{3/2}P$	−0.0293	−0.1521	−0.1892	−0.9671
j	mP^2	−7.874E-5	−1.957E-4	−1.973E-4	−7.503E-5
	mtP^2	3.382E-6	1.48E-5	3.02E-6	−8.45E-6
	mt^2P^2	−5.11E-8	−2.24E-7	8.78E-8	2.71E-7
validity range		0–40 °C, I = 0–1.0 *m*, 0–1000 bar	0–40 °C, I = 0–1.2 *m*, 0–1000 bar	0–40 °C, I = 0–1.2 *m*, 0–1000 bar	0–40 °C, I = 0–1.0 *m*, 0–1000 bar
$10^6\sigma$, bar^{-1}		0.006	0.006	0.006	0.006

Table III. Comparison of the Densities for NaCl Aqueous Solutions Determined in This Study and the Direct Measurements of Chen, Emmet, and Millero (*2*)

	I = 0.2014 *m*				I = 0.7232 *m*			
	0 °C		25 °C		0 °C		25 °C	
P, bar	Δd^a	Δ^b	Δd^a	Δ^b	Δd^a	Δ^b	Δd^a	Δ^b
0	8956	−5	8214	1	31 059	−26	28 672	−23
100	8844	65	8148	82	30 690	85	28 450	113
200	8735	87	8084	118	30 335	104	28 236	148
300	8631	82	8023	124	29 992	62	28 030	130
400	8530	60	7964	113	29 663	5	27 831	95
500	8434	33	7907	96	29 347	−46	27 640	57
600	8342	8	7852	79	29 045	−82	27 456	31
700	8254	−9	7799	70	28 757	−90	27 280	33
800	8170	−17	7749	67	28 483	−92	27 110	45
900	8091	−21	7700	71	28 222	−97	26 947	37
1000	8016	−21	7653	74	27 976	−162	26 790	−23
		av 37.1		av 81.4		av 77.4		av 66.8

[a] $\Delta d = [d(\text{soln}) - d(H_2O)]10^6$, where the densities (g cm^{-3}) are calculated from eq 7. [b] $\Delta = 10^6[d(\text{this study}) - d(\text{ref } 2)]$, g cm^{-3}.

(*12*). At higher pressures the values of A and B in eq 1 are also consistent with the pure-water values

$$A = A_0 + hm + im^{3/2} \tag{5}$$

$$B = B_0 + jm \tag{6}$$

where A_0 and B_0 for water are given elsewhere (*12*). The values of h, i, and j for the salts determined from the iterative computer program (*7*) over the ranges of 0–1 *m* ionic strength (I), 0–40 °C, and 0–1000 bar are given in Table II. The significance of the various terms is determined by using the F test (*7*, *14*). The maximum error of the equations of state is estimated to be $\pm 0.06 \times 10^{-6}$ bar^{-1} in isothermal compressibility. The precision of the specific volume is estimated to be better than $\pm 30 \times 10^{-6}$ cm^3 g^{-1}, and the thermal expansibility is estimated to be reliable to within $\pm 4 \times 10^{-6}$ deg^{-1}.

Results and Discussion

The densities (the reciprocal of the specific volume) of the four major sea-salt solutions at any concentration, temperature, and pressure over the ranges studied (0–1 *m* ionic strength, 0–40 °C, and 0–1000 bar) can be calculated from the rearranged form of eq 1.

$$d^P = d^0/(1 - p/K^P) \tag{7}$$

The isothermal compressibilities and the thermal expansibilities can be calculated by differentiating eq 7 with respect to pressure and temperature, respectively (*8*).

The densities of NaCl solutions at I = 0.2014 *m* (corresponding to 10‰ in seawater salinity) and I = 0.7232 *m* (35‰ in seawater salinity) calculated from eq 7 are compared with the work of Chen, Emmet, and Millero (*2*) in Table III. The

Table IV. Comparison of the Densities of NaCl Solutions Calculated from Eq 7 and the Data of Various Workers (*15-17*)

I, m	t, °C	P, bar	Δ^a	ref
0.1728	20	100.31	−165	*17*
0.1728	20	505.62	40	*17*
0.1728	20	1012.24	703	*17*
0.1	25	19.25	−65	*15*
0.2	25	19.25	−73	*15*
0.5	25	19.25	−197	*15*
1.0	25	19.25	−170	*15*
0.001	40	100.31	−98	*16*
0.01	40	100.31	−40	*16*
0.1	40	100.31	−258	*16*
1.0	40	100.31	−1002	*16*

[a] $\Delta = [d(\text{this study}) - d(\text{other worker})]10^6$, g cm^{-3}.

Table V. Comparison of Our Values of $\Delta\beta$ and Those Obtained by Millero et al. (*18*)

temp, °C	NaCl $\Delta\beta^a$	NaCl Δ^b	$MgCl_2$ $\Delta\beta^a$	$MgCl_2$ Δ^b	Na_2SO_4 $\Delta\beta^a$	Na_2SO_4 Δ^b	$MgSO_4$ $\Delta\beta^a$	$MgSO_4$ Δ^b
				$I = 0.2014\ m$				
0	1.59	0.00	0.93	0.00	1.41	0.02	0.90	0.04
25	1.04	−0.08	0.68	0.01	0.97	0.00	0.66	−0.00
				$I = 0.7232\ m$				
0	5.17	0.07	3.18	0.08	4.55	0.04	3.00	0.10
25	3.47	−0.19	2.32	0.05	3.22	0.04	2.21	−0.01

[a] $\Delta\beta = -10^6(\beta - \beta_0)$, bar^{-1}, obtained by differentiating eq 7 with respect to pressure. [b] $\Delta = [\Delta\beta(\text{this study}) - \Delta\beta(\text{ref } 18)]10^6$, bar^{-1}.

Table VI. Comparison of Our $\Delta\beta$ Values for NaCl and Those Obtained by Duedall (*19*)

	2 °C				15 °C			
	0.13 m		0.26 m		0.13 m		0.26 m	
P, bar	$\Delta\beta^a$	Δ^b	$\Delta\beta^a$	Δ^b	$\Delta\beta^a$	Δ^b	$\Delta\beta^a$	Δ^b
0	0.99	0.11	1.93	0.11	0.77	0.11	1.51	0.04
100.1	0.95	0.11	1.85	0.10	0.74	0.08	1.45	0.03
200.1	0.91	0.09	1.78	0.09	0.71	0.08	1.40	0.03
300.3	0.88	0.10	1.70	0.09	0.69	0.06	1.34	0.02
400.5	0.84	0.09	1.63	0.08	0.66	0.06	1.29	0.02
500.5	0.80	0.08	1.56	0.07	0.63	0.06	1.24	0.03
600.3	0.76	0.08	1.49	0.07	0.61	0.06	1.18	0.01
700.1	0.73	0.08	1.42	0.06	0.58	0.06	1.14	0.03
800.1	0.69	0.09	1.35	0.06	0.56	0.07	1.09	0.03
900.1	0.66	0.08	1.28	0.08	0.53	0.07	1.04	0.04

[a] $\Delta\beta = -10^6(\beta - \beta_0)$, bar^{-1}, obtained by differentiating eq 7 with respect to pressure. [b] $\Delta = [\Delta\beta(\text{this study}) - \Delta\beta(\text{ref } 19)]10^6$, bar^{-1}.

densities of the direct measurements (*2*) were estimated to be better than 100 × 10^{-6} g cm^{-3}. At $I = 0.2014\ m$, the two sets of data agree on the average to 37 × 10^{-6} and 81 × 10^{-6} g cm^{-3} at 0 and 25 °C, respectively. At $I = 0.2014\ m$, the two sets of data agree on the average to 37 × 10^{-6} and 81 × 10^{-6} g cm^{-3} at 0 and 25 °C, respectively. At $I = 0.7232\ m$, the average agreements are within 77 × 10^{-6} and 67 × 10^{-6} g cm^{-3} at 0 and 25 °C, respectively. The comparisons of eq 7 with the density data of other workers (*15-17*) show larger discrepancies (Table IV).

At 1 atm the isothermal compressibilities relative to pure water $\Delta\beta = (\beta - \beta_0)$ obtained in this study agree very well with the direct measurements of Millero et al. (*18*) from 0 to 45 °C at concentrations up to 1 m. The comparisons at 0 and 25 °C and $I = 0.2014$ and 0.7232 m are given in Table V. The agreement is comparable with the estimated accuracy of Millero et al., 0.07 × 10^{-6} bar^{-1}. In the high-pressure region, our results agree with the data of Duedall (*19*) to 0.11 × 10^{-6} bar^{-1} at 0.13 and 0.26 m, 2 and 15 °C, and up to 900 bar (Table VI).

Table VII. Comparison of Our Values of $\partial V/\partial P$ for NaCl with Those of Rowe and Chow (*20*) at 21.7 °C

	$I = 0\ m$		$I = 0.90056\ m$		
P, bar	$-\partial V/\partial P^a$	Δ^b	$-\partial V/\partial P^a$	Δ^b	Δ^c (I = 0.90056 m)
9.12	45.65	0.9_5	39.85	1.1_5	-0.2_0
100.29	44.41	0.6_9	38.83	0.9_7	-0.2_8
201.59	43.10	0.4_0	37.76	0.6_4	-0.2_4
302.89	41.84	0.0_6	36.73	0.3_7	-0.3_1

[a] The values of $(\partial V/\partial P)10^6$ were calculated from the differentiation of eq 7 with respect to pressure (cm^3 g^{-1} bar^{-1}). [b] $\Delta = 10^6[(\partial V/\partial P)(\text{this study}) - (\partial V/\partial P)(20)]$. [c] $\Delta = 10^6[(\partial V/\partial P)_0 - (\partial V/\partial P)_{NaCl}](\text{this study}) - 10^6[(\partial V/\partial P)_0 - (\partial V/\partial P)_{NaCl}](\text{ref } 20)$.

Table VIII. Comparison of the Densities for $MgCl_2$ Aqueous Solutions Determined in This Study and the Direct Measurements of Chen, Emmet, and Millero (*2*)

	$I = 0.2014\ m$				$I = 0.7232\ m$			
	0 °C		25 °C		0 °C		25 °C	
P, bar	Δd^a	Δ^b	Δd^a	Δ^b	Δd^a	Δ^b	Δd^a	Δ^b
0	5.537	−12	5.302	16	19.457	2	18.677	6
100	5.473	−4	5.258	9	19.236	32	18.529	44
200	5.411	−6	5.217	8	19.024	29	18.387	43
300	5.352	−8	5.177	6	18.820	11	18.251	29
400	5.295	−11	5.139	−3	18.625	−9	18.120	4
500	5.241	−12	5.102	−12	18.440	−28	17.994	−18
600	5.189	−8	5.067	−18	18.264	−36	17.874	−16
700	5.141	1	5.033	−21	18.098	−33	17.758	−50
800	5.095	12	5.000	−23	17.941	−22	17.646	−62
900	5.052	23	4.968	−26	17.795	−1	17.538	−78
1000	5.012	35	4.937	−33	17.659	−2	17.434	−109
		av 12		av 17		av 19		av 42

[a] $\Delta d = [d(\text{soln}) - d(H_2O)]10^3$, where the densities (g cm^{-3}) are calculated from eq 7. [b] $\Delta = 10^6 \Delta d(\text{this work}) - 10^6 \Delta d(\text{ref } 2)$.

The agreement is within the combined precision of the two studies.

Rowe and Chou (*20*) measured the derivatives $\partial V/\partial P$ of NaCl solutions over wide concentration, temperature, and pressure ranges. Their results at 21.7 °C and $m = 0$ and 0.9 are compared with our data in Table VII. The maximum difference in $\partial V/\partial P$ is 1.15 × 10^{-6} cm^3 g^{-1} bar^{-1}, which is comparable with the estimated accuracy of Rowe and Chou, 3% of the true $\partial V/\partial P$ values. The values of $\partial V/\partial P$ in NaCl relative to pure water, $(\partial V/\partial P)_0 - (\partial V/\partial P)_{NaCl}$, of the two studies show a better agreement. The average difference is less than 0.3 × 10^{-6} cm^3 g^{-1} bar^{-1}.

Little work has been done on the 1-atm compressibility and high-pressure *PVT* properties for $MgCl_2$, Na_2SO_4, and $MgSO_4$ aqueous solutions except that measured previously in our laboratory using different techniques (*2*, *18*) and the work of Duedall (*19*). The 1-atm sound speeds determined relative to 1-atm compressibilities calculated from eq 3 are compared with the direct measurements of Millero et al. (*18*) in Table V. The agreement is within the combined precision of the two studies.

At high pressures, the densities of $MgCl_2$ aqueous solutions calculated from eq 7 agree with the direct measurements of Chen, Emmet, and Millero (*2*) to within ±42 × 10^{-6} g cm^{-3} at $I = 0.2014$ and 0.7232 m (0 and 25 °C) (Table VIII). The densities for Na_2SO_4 solutions determined in this study agree with the direct measurements to within ±33 × 10^{-6} g cm^{-3} at $I = 0.2014\ m$. At $I = 0.7232\ m$, the deviations are larger (Table IX, ±73 × 10^{-6} and ±140 × 10^{-6} g cm^{-3} at 0 and 25 °C, respectively). The sound-determined densities for $MgSO_4$ aqueous solutions are higher than the direct measurements (Table X, average 236 × 10^{-6} g cm^{-3} at $I = 0.7232\ m$ and 25 °C).

It is suspected that in a few cases the magnetic float used in our earlier direct measurements (*1*, *2*) may not have reached

Table IX. Comparison of the Densities for Na_2SO_4 Aqueous Solutions Determined in This Study and the Direct Measurements of Chen, Emmet, Millero (*2*)

	$I = 0.2014\ m$				$I = 0.7232\ m$			
	0 °C		25 °C		0 °C		25 °C	
P, bar	Δd^a	Δ^b	Δd^a	Δ^b	Δd^a	Δ^b	Δd^a	Δ^b
0	9.168	−4	8.526	3	31.896	48	29.862	7
100	9.074	4	8.468	15	31.591	110	29.669	81
200	8.981	0	8.411	19	31.294	146	29.482	125
300	8.890	−8	8.356	19	31.003	149	29.300	147
400	8.802	−20	8.302	17	30.720	132	39.124	152
500	8.716	−34	8.250	12	30.445	112	28.953	153
600	8.633	−45	8.200	11	30.178	83	28.787	154
700	8.553	−54	8.151	11	29.920	60	28.626	156
800	8.475	−63	8.103	14	29.671	39	28.470	169
900	8.400	−67	8.057	21	29.431	24	28.319	186
1000	8.320	−68	8.012	29	29.201	9	28.172	207
		av 33		av 16		av 73		av 140

^{a} $\Delta d = [d(\text{soln}) - d(H_2O)]10^3$, where the densities (g cm^{-3}) are calculated from eq 7. ^{b} $\Delta = 10^6\Delta d(\text{this work}) - 10^6\Delta d(\text{ref } 4)$.

Table X. Comparison of the Densities for $MgSO_4$ Aqueous Solutions Determined in This Study and the Direct Measurements of Chen, Emmet, and Millero (*2*)

	$I = 0.2014\ m$				$I = 0.7232\ m$			
	0 °C		25 °C		0 °C		25 °C	
P, bar	Δd^a	Δ^b	Δd^a	Δ^b	Δd^a	Δ^b	Δd^a	Δ^b
0	6.418	−10	6.142	2	22.501	25	21.607	0
100	6.360	48	6.104	70	22.312	122	21.481	145
200	6.304	89	6.067	117	22.126	195	21.357	236
300	6.249	115	6.030	141	21.946	231	21.237	289
400	6.195	180	5.994	153	21.770	243	21.121	310
500	6.141	128	5.959	151	21.599	234	21.007	308
600	6.090	126	5.925	141	21.433	220	20.897	291
700	6.039	120	5.891	125	21.272	205	20.790	266
800	5.989	116	5.858	107	21.116	205	20.687	239
900	5.941	117	5.826	91	20.965	228	20.587	246
1000	5.894	127	5.794	82	20.819	278	20.491	270
		av 107		av 107		av 199		av 236

^{a} $\Delta d = [d(\text{soln}) - d(H_2O)]10^3$, where the densities (g cm^{-3}) are calculated from eq 7. ^{b} $\Delta = 10^6\Delta d(\text{this work}) - 10^6\Delta d(\text{ref } 4)$.

Table XI. Comparison of Our $\Delta\beta$ Values for $MgCl_2$ and Those Obtained by Duedall (*19*)

	2 °C				15 °C			
	0.13 m		0.26 m		0.13 m		0.26 m	
P, bar	$\Delta\beta^a$	Δ^b	$\Delta\beta^a$	Δ^b	$\Delta\beta^a$	Δ^b	$\Delta\beta^a$	Δ^b
0	1.70	0.18	3.29	0.09	1.41	0.16	2.74	0.14
100.1	1.63	0.17	3.15	0.07	1.35	0.15	2.62	0.10
200.1	1.56	0.16	3.01	0.06	1.30	0.14	2.51	0.07
300.3	1.49	0.15	2.88	0.06	1.24	0.12	2.40	0.04
400.5	1.42	0.15	2.74	0.06	1.19	0.12	2.30	0.02
500.5	1.35	0.14	2.61	0.07	1.14	0.12	2.21	0.01
600.3	1.29	0.15	2.48	0.08	1.09	0.11	2.11	0.00
700.1	1.22	0.15	2.35	0.09	1.05	0.12	2.02	0.00
800.1	1.15	0.15	2.23	0.12	1.01	0.13	1.94	0.00
900.1	1.09	0.15	2.10	0.14	0.96	0.13	1.86	0.01

^{a} $\Delta\beta = -(\beta - \beta_0)10^6$, bar^{-1}. ^{b} $\Delta = [\Delta\beta(\text{this study}) - \Delta\beta(\text{ref } 19)]10^6$, bar^{-1}.

Table XII. Comparison of Our $\Delta\beta$ Values for Na_2SO_4 and Those Obtained by Duedall (*19*)

	2 °C				15 °C			
	0.13 m		0.26 m		0.13 m		0.26 m	
P, bar	$\Delta\beta^a$	Δ^b	$\Delta\beta^a$	Δ^b	$\Delta\beta^a$	Δ^b	$\Delta\beta^a$	Δ^b
0	2.50	0.07	4.68	−0.04	2.02	0.01	3.82	−0.02
100.1	2.43	0.07	4.53	−0.03	1.96	0.01	3.70	−0.04
200.1	2.35	0.05	4.39	−0.05	1.90	0.01	3.58	−0.06
300.3	2.28	0.05	4.25	−0.04	1.84	0.01	3.46	−0.10
400.5	2.20	0.04	4.10	−0.04	1.78	0.02	3.35	−0.09
500.5	2.12	0.04	3.96	−0.02	1.72	0.02	3.24	−0.10
600.3	2.04	0.03	3.82	0.00	1.66	0.03	3.13	−0.10
700.1	1.97	0.04	3.68	0.02	1.60	0.04	3.02	−0.11
800.1	1.89	0.03	3.53	0.03	1.55	0.06	2.92	−0.10
900.1	1.82	0.05	3.39	0.08	1.49	0.07	2.81	−0.09

^{a} $\Delta\beta = -(\beta - \beta_0)10^6$, bar^{-1}. ^{b} $\Delta = [\Delta\beta(\text{this study}) - \Delta\beta(\text{ref } 19)]10^6$, bar^{-1}.

Table XIII. Comparison of Our $\Delta\beta$ Values for $MgSO_4$ and Those Obtained by Duedall (*19*)

	2 °C				15 °C			
	0.13 m		0.26 m		0.13 m		0.26 m	
P, bar	$\Delta\beta^a$	Δ^b	$\Delta\beta^a$	Δ^b	$\Delta\beta^a$	Δ^b	$\Delta\beta^a$	Δ^b
0	2.12	0.03	4.02	0.03	1.76	0.02	3.36	0.03
100.1	2.06	0.03	3.89	0.01	1.71	0.01	3.26	0.02
200.1	1.99	0.02	3.75	−0.01	1.67	0.02	3.15	0.00
300.3	1.93	0.02	3.62	−0.02	1.62	0.02	3.05	−0.01
400.5	1.87	0.02	3.50	−0.02	1.57	0.01	2.94	−0.03
500.5	1.81	0.03	3.37	−0.03	1.52	0.01	2.84	−0.03
600.3	1.75	0.03	3.25	−0.02	1.47	0.01	2.74	−0.04
700.1	1.69	0.04	3.13	−0.01	1.42	0.01	2.64	−0.04
800.1	1.63	0.05	3.01	0.01	1.37	0.01	2.54	−0.04
900.1	1.57	0.06	2.89	0.03	1.33	0.02	2.45	−0.03

^{a} $\Delta\beta = -(\beta - \beta_0)10^6$, bar^{-1}. ^{b} $\Delta = [\Delta\beta(\text{this study}) - \Delta\beta(\text{ref } 19)]10^6$, bar^{-1}.

equilibrium after each pressure change before the data were taken. This may have contributed to the relatively large difference between the sound-derived and directly measured densities for $MgSO_4$ and also for Na_2SO_4 at $I = 0.7232\ m$ and 25 °C. The error caused by the sound absorption is probably small except in the case of $MgSO_4$ (*21–23*).

The absorption of sound in $MgSO_4$ solutions increases the sound speeds. The positive shift, or dispersion, in sound speed (ΔU) caused by relaxation can be estimated from eq 8 and 9

$$\Delta U = U_f - U_0 \tag{8}$$

$$= (\alpha_{\max}/\pi)U_\infty(f/f_R)^2/[1 + (f/f_R)^2] \tag{9}$$

(*24*), where U_f is the sound speed at frequency f (with absorption), U_0 is the sound speed at zero frequency (no absorption), $\alpha_{\max}$ is the absorption per wavelength at the relaxation frequency, f_R is the relaxation frequency, and U_∞ is the sound speed at infinite frequency. It has been estimated by Millero et al. (*23*) that at a concentration of 0.5 m, the sound wave of 2-MHz frequency used in this study gives a value of $\Delta U = 1.0$ m s^{-1} in $MgSO_4$ solutions. The shift of sound speed over the concentration range of this study (up to 0.25 m) is less than 1.0 m s^{-1}. Even a correction of 1.0 m s^{-1} will only increase the isothermal compressibility by ~0.06 × 10^{-6} bar^{-1}, which is equal to an increase of ~60 × 10^{-6} g cm^{-3} in density at 1000 bar. This correction would increase the density difference between the sound-derived densities of $MgSO_4$ solution and the direct measurements at 1000 bar.

Recently, Duedall (*19*) constructed a bellows-type differential compressimeter to measure directly, to 900 bar, the differences between the isothermal compressibilities of many sea salts and distilled, deionized water at 2 and 15 °C. The precision is better than ±0.07 × 10^{-6} bar^{-1} over the pressure range of 0–900 bar. It has been shown earlier that his results for NaCl agree with our work to better than 0.11 × 10^{-6} bar^{-1} over the range of his study, which is within the combined precision of the two studies. In Tables XI–XIII, we have compared our results for $MgCl_2$, Na_2SO_4, and $MgSO_4$ with the data of Duedall (*19*).

The largest deviation between the two studies is for $MgCl_2$ solutions. Our $\Delta\beta$ values are consistently higher than those of

Duedall by as much as 0.18×10^{-6} bar^{-1} at 2 °C and 0.13 m. The difference in $\Delta\beta$, if integrated over the pressure range at 2 °C and 0.13 m, would indicate that the density of Duedall is $\sim 150 \times 10^{-6}$ g cm^{-3} higher than our value at 900 bar. Since our density is only 23×10^{-6} g cm^{-3} higher than that of Chen, Emmet, and Millero, which is well within the combined precision of these two studies, we suspect that the work of Duedall may have been subjected to some systematic error for $MgCl_2$ solutions.

The agreement of our $\Delta\beta$ data for Na_2SO_4 and $MgSO_4$ with the data of Duedall is well within the combined precision of the two studies. The good agreement substantiates the validity of our sound-derived equations and suggests that the direct density measurement of Chen, Emmet, and Millero (*2*) for $MgSO_4$ may be too low.

In summary, we have presented what we feel are the best available high-pressure properties for NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ solutions from 0 to 1000 bar, 0 to 40 °C, and 0 to 1 m.

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Solubilities of Vinyl Chloride and Vinylidene Chloride in Water

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A review of the published data for the solubilities of vinyl chloride and vinylidene chloride in water is presented, and data from new experiments are offered. A consensus existed among the vinyl chloride data sources. Our new data agreed with the majority position. The solubility of vinyl chloride in water was found to be nearly constant at 0.95 wt % over the range 15–85 °C. Little vinylidene chloride data have been published, and no consensus existed. Our data showed the solubility of vinylidene chloride in water to be nearly constant at 0.25 wt % over the range 15–90 °C.

Introduction

The solubilities of vinyl chloride and vinylidene chloride in water are valuable data for understanding any process which involves water and either of these monomers. They are especially important for the polymerization and finishing of homopolymers or copolymers of these monomers. The purpose of this paper is to provide this valuable solubility information in one place.

Vinyl Chloride. A Review

Six sources of vinyl chloride solubility data were found. Gerrens et al. (*1*) reported the solubility of vinyl chloride in water to be 1 g/100 mL, or 1.0 wt %, at 50 °C. The value was given without explanation or reference.

Hayduk and Laudie (*2*) reported extensive studies of the vinyl chloride–water system. Their solubility experiments were performed over a wide range of temperatures. Although they did not directly measure the solubility of vinyl chloride in water at the vapor pressure of vinyl chloride, they were able to extrapolate. They started with a known volume and partial pressure of vinyl chloride in a thermostatted bomb. They introduced a known amount of water to the bomb and adjusted the volume of the bomb to maintain the starting pressure. The vinyl chloride lost from the vapor phase was assumed to have dissolved in water. At 0.2, 25, 50, and 75 °C, they performed experiments at two or more vinyl chloride partial pressures. These data were then extrapolated to the vapor pressure of vinyl chloride by using a general form of Henry's law, eq 1,

$$P = H'C^{k} \qquad (1)$$

where P is the partial pressure (or vapor pressure) of vinyl chloride, H' is a solubility coefficient which is exactly the Henry's law coefficient when $k = 1$, C is the concentration of vinyl chloride in the water, and k is an adjustable parameter. Restatement of their data gives the solubility of vinyl chloride in water as 0.90 wt % at 0.2 °C, 0.87 wt % at 25 °C, 1.01 wt % at 50 °C, and 1.28 wt % at 75 °C.

Berens (*3*) reported the solubility of vinyl chloride in water at 30 and 50 °C. He determined the solubility of vinyl chloride by measuring the pressure at apparent equilibrium in a stirred,

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