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The Apparent Molal Volumes of Aqueous Solutions of $NaCl$, KCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ from 0 to 1000 Bars at 0, 25, and 50 °C†

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The densities of aqueous solutions of $NaCl$, KCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ have been measured with a high pressure magnetic float densimeter from 0 to 1000 bars, 0.01 to 1.0 m ionic strength, and at 0, 25, and 50 °C. The relative apparent molal volumes, $\phi_V(P) - \phi_V(0)$, of these solutions have been fitted to an equation of the form $\phi_V(P) - \phi_V(0) = \phi_V^0(P) - \phi_V^0(0) + Sm^{1/2}$ where the relative infinite dilution partial molal volumes, $\phi_V^0(P) - \phi_V^0(0)$, and the slopes S are functions of applied pressure and temperature. The pressure, temperature, and concentration dependence of the apparent molal volumes are briefly discussed.

Although there are reliable density and apparent molal volume data for many electrolytes at 1 atm (*9, 11*), little reliable data are available at high pressures. In our recent studies of the volume properties of multicomponent electrolyte solutions (*13, 15*) we have been examining the use of Young's rule (*18*) in predicting the properties of seawater. In order to predict the apparent molal volumes of seawater at elevated pressures (*3*), we had a need for reliable volume data on sea salts ($NaCl$, KCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$). The present paper contains results on the apparent molal volumes of these salts from 0 to 1000 bars applied pressure, 0.01 to 1.0 ionic strength (to 2.0 ionic strength for $NaCl$), and 0, 25, and 50 °C.

Experimental Section

The high pressure magnetic float densimeter used in this study is described in detail elsewhere (*12*). The high pressure densimeter consists essentially of a 1 atm densimeter (*8*) enclosed in a nonmagnetic bomb with optical ports to observe the motion of the float. The apparatus consists of a pressure bomb, a magnetic float, and auxiliary measuring and control systems.

The pressure bomb used in this study was machined from beryllium copper. The cylindrical bomb contains two plugs seated with O rings to form a vessel of 170 cm^3. The magnetic float is made of thick-wall (0.4 cm) Pyrex glass and contains an Alnico-5 bar magnet. The volume of the float is 58.7672 cm^3 at 0 °C and 1 atm.

The pressure bomb was completely immersed in a 30-L constant temperature bath controlled to ±0.001 °C with a Hallikainen Thermotrol. The temperature of the bath was set to ±0.005 °C with a platinum resistance thermometer (calibrated by the National Bureau of Standards, 1968 temperature scale). A 2800-bar Enerpac hand pump was used to generate pressure. A 1400-bar Heise Bourdon tube gauge was used to set the pressure. The Heise gauge was calibrated with a Harwood Engineering deadweight tester. The pressures were found to be reproducible to ±0.5 bars from 0 to 1000 bars and are thought to be accurate to 1.4 bars.

Ion-exchanged (18 MΩ) water (Millipore-Super Q system) was used in the calibration runs and in the preparation of the solutions. Reagent grade salts were used, without further purification, for preparation of the solutions. The solutions of $NaCl$, KCl, Na_2SO_4, and $MgSO_4$ were analyzed by evaporation to dryness. The $MgCl_2$ solutions were analyzed gravimetrically with $AgNO_3$.

The calibration of the densimeter (*2, 3*) was made with ion-exchanged water using the densities of water from the sound-derived equation of state (*4*). The calibration results (*2*) indicate that the precision of the densities is ±3 ppm at a given temperature and ±8 ppm over the entire temperature range. The accuracy of the densities is thought to be ~30 ppm at 1000 bars applied pressure. An error of ±30 ppm in density is equivalent to an error of ± 0.3 cm^3 mol^{-1} at 0.1 m and ± 0.03 cm^3 mol^{-1} at 1.0 m in ϕ_V for 1–1 electrolytes.

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† Taken in part from the dissertation submitted by Robert T. Emmet in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Miami.

Table I. The Apparent Molal Volumes of Aqueous Salt Solutions as a Function of Concentration and Pressure at 0 °C

	ϕ_V(NaCl)							
P, bar	m = 0.03027	m = 0.1299	m = 0.2507	m = 0.3852	m = 0.7766	m = 0.9630	m = 1.307	m = 2.008
0.00[a]	13.209	13.607	13.952	14.279	15.089	15.436	16.040	17.182
99.90	14.998	14.871	15.149	14.899	15.796	16.049	—	17.680
199.80	15.706	—	15.818	15.324	—	16.632	17.121	18.159
300.20	16.697	15.929	16.450	15.768	16.827	—	—	—
401.00	17.281	16.375	16.954	16.009	17.335	17.713	18.096	19.044
501.10	—	16.738	17.464	—	17.880	18.202	18.531	—
601.00	17.530	17.203	17.996	—	18.230	18.664	19.935	19.829
701.60	18.176	17.635	18.438	—	18.647	19.101	19.353	20.185
802.00	18.246	17.970	18.935	—	19.032	19.510	19.728	20.528
901.70	18.579	18.244	19.250	—	19.420	19.877	20.066	20.840
1001.20	18.878	—	19.655	—	19.757	—	20.406	21.136

	ϕ_V(KCl)					
P, bar	m = 0.1655	m = 0.3331	m = 0.5009	m = 0.6693	m = 0.8360	m = 1.0040
0.00[a]	24.407	24.853	25.244	25.609	25.949	26.280
196.62	—	26.280	26.573	26.856	26.976	27.267
396.29	27.326	27.275	27.538	27.806	27.871	28.123
595.97	27.605	28.129	28.369	28.601	28.651	28.873
795.65	—	28.857	29.086	29.309	29.331	29.536
895.49	29.380	—	—	—	—	—
995.33	—	29.498	29.716	29.897	29.930	—

	ϕ_V($MgCl_2$)						
P, bar	m = 0.00876	m = 0.03505	m = 0.07877	m = 0.07937	m = 0.1395	m = 0.2184	m = 0.3150
0.00[a]	11.174	11.914	12.638	12.646	13.343	14.041	14.726
99.90	12.568	13.305	13.937	14.010	15.786	15.326	16.024
199.80	12.568	14.598	15.059	—	16.890	16.425	17.132
300.20	15.704	15.980	—	16.776	17.890	—	18.208
401.00	15.392	16.980	17.545	17.905	17.983	18.520	19.192
501.10	15.800	17.433	18.349	18.162	18.875	19.274	20.059
601.00	18.424	18.822	19.296	19.649	—	20.215	20.969
701.60	—	19.999	20.189	20.658	20.780	21.114	21.804
802.00	20.561	—	21.332	21.677	21.730	21.799	—
901.70	—	—	22.336	22.580	22.580	22.652	23.322
1001.20	—	—	22.955	22.973	23.446	23.336	—

	ϕ_V(Na_2SO_4)				
P, bar	m = 0.00899	m = 0.0832	m = 0.1480	m = 0.2312	m = 0.3335
0.00[a]	3.227	5.809	7.467	9.371	11.536
99.90	5.110	8.214	9.898	11.699	13.440
199.80	—	9.692	11.740	13.439	15.083
300.20	—	11.641	—	15.100	16.698
401.00	—	13.022	15.254	16.786	18.175
501.10	11.805	14.365	16.626	18.175	19.576
601.00	13.933	15.781	18.103	19.475	20.960
701.60	14.391	17.068	19.474	20.954	22.219
802.00	16.562	18.291	20.853	22.128	23.471
901.70	18.219	19.517	22.177	23.218	24.652
1001.20	—	—	23.255	24.419	25.676

	ϕ_V($MgSO_4$)				
P, bar	m = 0.01985	m = 0.05328	m = 0.1029	m = 0.1693	m = 0.2503
0.00[a]	−9.081	−7.159	−5.568	−4.172	−2.881
196.62	−2.095	—	—	—	—
296.95	—	—	—	—	—
396.29	1.140	2.000	2.686	3.432	3.447
496.13	—	—	—	—	—
595.97	3.599	7.755	5.501	6.082	6.054
695.81	—	—	—	—	—
795.65	6.455	7.755	8.208	8.507	8.444
895.49	—	—	—	—	—
995.33	9.604	10.191	10.496	10.762	—

[a] The values of ϕ_V have been normalized to the best available literature values calculated from eq 3.

Table II. The Apparent Molal Volumes of Aqueous Salt Solutions as a Function of Concentration and Pressure at 25 °C

$\phi_V(\mathrm{NaCl})$

P, bar	m = 0.1299	m = 0.2507	m = 0.3852	m = 0.7766	m = 0.9630	m = 1.3070	m = 2.008
0.00[a]	17.289	17.547	17.765	18.237	18.416	18.705	19.189
99.90	18.493	18.536	18.446	18.583	18.738	19.044	19.536
199.80	18.764	18.898	18.820	—	19.104	19.374	19.853
300.20	19.294	19.332	19.171	—	19.451	19.700	20.145
401.00	19.517	19.681	19.478	19.565	19.799	20.009	20.439
501.10	19.757	19.988	19.785	19.844	—	20.284	20.704
601.00	20.157	20.294	20.083	20.135	20.417	20.566	20.956
701.60	—	20.625	20.373	20.434	20.695	20.827	21.195
802.00	20.693	20.847	20.641	20.714	20.972	21.066	21.428
901.70	20.938	—	20.877	20.953	21.233	21.304	21.645
1001.20	31.133	—	21.131	—	21.462	21.524	—

$\phi_V(\mathrm{KCl})$

P, bar	m = 0.3331	m = 0.5009	m = 0.6693	m = 0.8360	m = 1.0040
0.00[a]	27.935	28.193	28.415	28.610	28.791
196.62	28.873	29.104	29.258	29.249	29.467
396.29	29.470	29.670	29.867	29.804	30.000
595.97	29.985	30.189	30.319	30.287	30.465
795.65	30.434	30.628	30.752	30.712	30.896
995.33	30.789	31.015	31.137	31.080	31.257

$\phi_V(\mathrm{MgCl_2})$

P, bar	m = 0.00876	m = 0.03505	m = 0.2184	m = 0.3150
0.00[a]	15.172	15.781	17.162	17.477
99.90	15.970	16.596	18.058	18.476
199.80	—	17.140	18.825	19.250
300.20	16.460	18.454	19.587	19.967
401.00	16.664	18.812	21.199	20.692
501.10	—	19.484	20.839	21.324
601.00	—	19.806	21.537	21.977
701.60	19.437	20.239	22.111	22.587
802.00	21.241	21.693	22.640	23.129
901.70	—	22.446	23.241	—
1001.20	—	22.385	23.704	24.157

$\phi_V(\mathrm{Na_2SO_4})$

P, bar	m = 0.0832	m = 0.1480	m = 0.2312	m = 0.3335
0.00[a]	14.963	16.095	17.234	18.388
99.90	16.508	17.711	19.130	20.352
199.80	17.767	18.902	20.311	21.454
300.20	18.994	—	21.481	22.564
401.00	20.150	21.232	22.544	23.569
501.10	21.328	22.218	23.558	24.553
601.00	22.412	23.311	24.568	25.548
701.60	23.435	24.299	25.560	—
802.00	24.569	25.332	26.494	27.394
901.70	—	26.255	27.415	—
1001.20	—	27.268	28.318	29.121

$\phi_V(\mathrm{MgSO_4})$

P, bar	m = 0.01985	m = 0.05328	m = 0.1029	m = 0.1693	m = 0.2503
0.00[a]	−3.402	−1.833	−0.660	0.346	1.375
96.79	—	—	—	—	—
196.62	1.861	3.089	3.653	4.598	4.351
296.45	—	—	—	—	—
396.29	4.569	5.626	—	6.774	6.443
496.13	—	—	—	—	—
595.97	6.614	7.840	8.008	8.777	8.395
695.81	—	—	—	—	—
795.65	7.543	9.769	9.864	10.580	10.150
895.49	—	—	—	—	—
995.33	9.148	11.431	11.570	12.204	11.801

[a] The values of ϕ_V have been normalized to the best available literature value calculated from eq 3.

Table III. The Apparent Molal Volumes of Aqueous Salt Solutions as a Function of Concentration and Pressure at 50 °C

	ϕ_V(NaCl)					
P, bar	m = 0.1299	m = 0.2507	m = 0.3852	m = 0.7766	m = 0.9630	m = 1.307
0.00[a]	18.610	18.865	19.060	19.416	19.527	19.677
99.90	19.718	19.545	19.648	19.917	19.838	19.954
199.80	20.090	—	19.942	20.203	20.137	20.232
300.20	20.438	20.125	20.242	—	20.422	20.492
401.00	20.698	20.393	20.533	20.731	20.705	20.950
501.10	20.858	20.686	20.793	20.987	20.971	—
601.00	21.154	21.029	21.048	21.205	21.224	21.223
701.60	21.339	21.348	21.306	21.448	21.470	21.442
802.00	21.607	21.601	21.612	21.699	—	21.666
901.70	21.742	21.964	21.881	21.893	—	21.868
1001.20	21.938	22.253	22.114	22.126	—	—

	ϕ_V(KCl)				
P, bar	m = 0.3331	m = 0.5009	m = 0.6693	m = 0.8360	m = 1.0040
0.00[a]	28.869	29.134	29.350	29.533	29.694
196.62	29.757	29.968	30.125	30.110	30.303
396.29	30.235	30.432	30.585	30.547	30.735
595.97	—	30.849	30.988	30.939	31.123
795.65	31.046	—	31.350	31.281	31.464
995.33	31.350	31.580	31.661	31.595	31.770

	ϕ_V(MgCl$_2$)			
P, bar	m = 0.07937	m = 0.1395	m = 0.2184	m = 0.3150
0.00[a]	15.621	16.229	16.792	17.295
99.90	16.634	17.619	18.023	18.317
199.80	17.238	18.261	18.717	19.028
300.20	18.105	18.974	19.454	19.747
401.00	18.512	19.546	20.118	20.353
501.10	19.185	20.206	20.709	21.010
601.00	19.916	20.645	21.356	21.602
701.60	20.544	21.246	21.917	—
802.00	20.844	21.755	22.531	22.705

	ϕ_V(Na$_2$SO$_4$)					
P, bar	m = 0.00899	m = 0.0367	m = 0.0832	m = 0.1480	m = 0.2312	m = 0.3335
0.00[a]	15.256	16.428	17.584	18.714	19.826	20.925
99.90	—	16.478	18.726	19.787	20.905	21.982
199.80	16.371	17.563	19.717	20.849	21.904	22.975
300.20	18.017	—	20.918	21.810	22.910	23.912
401.00	19.114	19.650	—	22.679	23.847	24.779
501.10	—	20.563	22.703	23.630	24.705	25.624
601.00	—	21.341	23.567	24.487	25.516	26.440
701.60	22.358	22.503	24.323	25.329	26.365	27.230
802.00	22.799	22.997	—	26.129	27.075	28.008

	ϕ_V(MgSO$_4$)				
P, bar	m = 0.01985	m = 0.05328	m = 0.1029	m = 0.1693	m = 0.2503
0.00[a]	−2.861	−1.053	0.073	0.973	2.068
196.62	2.783	4.211	4.564	5.191	5.025
396.29	6.012	6.784	6.764	7.185	6.933
496.13	—	—	—	—	—
595.97	8.345	8.730	8.500	8.979	8.643
695.81	—	—	—	—	—
795.65	9.496	10.229	9.904	10.515	10.140
895.49	—	—	—	—	—
995.33	9.979	—	11.420	11.777	11.535

[a] The values of ϕ_V have been normalized to the best available literature values calculated from eq 3.

Results and Discussion

The densities of aqueous solutions of NaCl, KCl, MgCl$_2$, Na$_2$SO$_4$, and MgSO$_4$ have been measured (*2*) from 0.01 to 1.0 ionic strength with a high pressure densimeter. The measurements were made from 0 to 1000 bars (in 100 bar increments) and at 0, 25, and 50 °C. The apparent molal volumes have been determined from these densities (d) by using the equation

$$\phi_V = \frac{1000(d^0 - d)}{dd^0 m} + \frac{M}{d} \qquad (1)$$

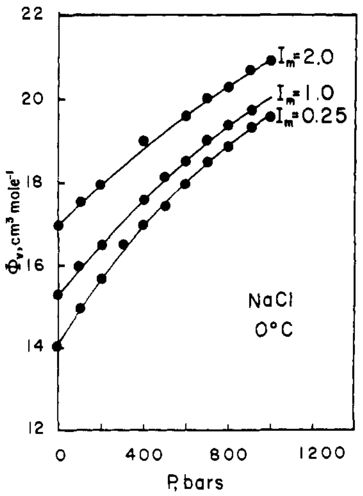

Figure 1. Apparent molal volumes of NaCl as functions of pressure at various concentrations and 0 °C.

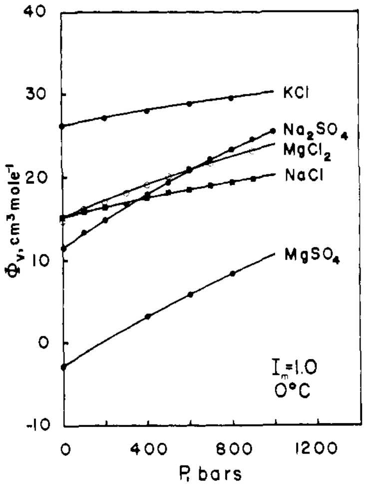

Figure 2. Apparent molal volumes of NaCl, KCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ as functions of pressure at I_m = 1 and 0 °C.

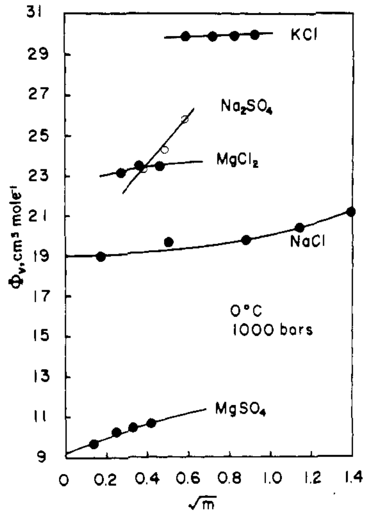

Figure 3. Apparent molal volumes of NaCl, KCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ as functions of $m^{1/2}$ at 0 °C and 1000 bars.

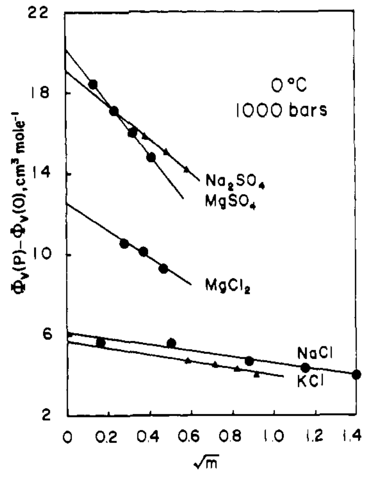

Figure 4. Relative apparent molal volumes, $\phi_V(P) - \phi_V(0)$, for NaCl, KCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ as functions of $m^{1/2}$ at 0 °C and 1000 bars.

where d^0 is the density of water (*4*), m is the molality of the solution, and M is the molecular weight of the salt. The values of ϕ_V determined from eq 1 are given in Tables I, II, and III for various solutions. Since the ϕ_V's for NaCl solutions have been obtained over the largest concentration range (0.03 to 2 m), we have examined the pressure and concentration dependence in Figure 1. The values of ϕ_V for NaCl at various molal ionic strengths, I_m, are plotted vs. pressure. The ϕ_V's increase with increasing pressure over the entire concentration range studied. At low molalities the ϕ_V's show a nonlinear pressure dependence, while at higher molalities the ϕ_V's have a near linear pressure dependence. This behavior is similar at each temperature for all of the electrolytes studied (see Figure 2).

Although the concentration dependences for some of the electrolytes studied are not linear functions of $m^{1/2}$ at a given pressure (Figure 3), the relative apparent molal volumes, $\phi_V(P) - \phi_V(0)$, are linear functions of $m^{1/2}$ (see Figure 4). Since the high pressure magnetic float system was designed to study the pressure effect on the densities or apparent molal volumes, we examined the relative apparent molal volumes as a function of applied pressure P (at $P = 0$, the absolute pressure is 1 atm), temperature (°C), and concentration (m, mol/kg of H_2O) by using the linear equation

$$\phi_V(P) - \phi_V(0) = \phi_V{}^0(P) - \phi_V{}^0(0) + Sm^{1/2} \qquad (2)$$

where $\phi_V(P)$ and $\phi_V(0)$ are the apparent molal volumes at applied pressure, P and 0; the superscript zero is used to denote infinite dilution; and S is an empirical parameter that varies with pressure and temperature. The relative infinite dilution apparent molal volumes and the parameter S were fitted by using a least-squares method to equations of the form

$$\phi_V{}^0(P) - \phi_V{}^0(0) = \sum_{i,j}^{n} a_{i,j}P^it^j \qquad (2a)$$

$$S = \sum_{i,j}^{n} b_{i,j}P^it^j \qquad (2b)$$

The coefficients needed for eq 2a and 2b were arrived at by fitting the data on an UNIVAC 1106 computer. These coefficients are given in Table IV along with the standard deviations.

In order to calculate the ϕ_V at a given P, t, and m from these equations, it is necessary to have reliable ϕ_V data at 1 atm or $P = 0$. The "best" available literature values for the 1 atm apparent molal volumes have been selected (*1, 5-7, 10, 14, 17*) and were fitted to the equation

$$\phi_V(0) = \phi_V{}^0(0) + Am^{1/2} + Bm + Cm^{3/2} \qquad (3)$$

where $\phi_V{}^0(0)$, A, B, and C are all temperature dependent parameters

Table IV. Coefficients for Equation 2[a]

Variables	NaCl	KCl	$MgCl_2$	Na_2SO_4	$MgSO_4$
P	1.542 (E − 2)	1.228 (E − 2)	1.566 (E − 2)	2.285 (E − 2)	4.076 (E −2)
Pt	−1.099 (E − 4)	−1.589 (E −4)	−3.150 (E − 4)	−3.141 (E − 4)	−2.901 (E − 4)
Pt^2	9.68 (E − 7)	1.797 (E − 6)	3.911 (E − 6)	2.125 (E − 6)	5.888 (E − 6)
$Pm^{1/2}$	−7.62 (E − 3)	−6.964 (E − 3)	−2.269 (E − 3)	−1.576 (E − 3)	−3.887 (E − 2)
$Ptm^{1/2}$	3.05 (E − 6)	7.060 (E − 5)	2.611 (E − 4)	1.257 (E − 4)	3.066 (E − 4)
$Pt^2m^{1/2}$	0	−9.849 (E − 7)	−3.115 (E − 6)	−1.597 (E − 6)	−9.099 (E − 6)
P^2	−2.439 (E − 5)	−1.261 (E − 5)	−1.202 (E − 5)	−1.250 (E − 5)	−3.593 (E − 5)
P^2t	1.81 (E − 8)	1.19 (E − 8)	1.19 (E − 8)	6.92 (E − 8)	−1.273 (E − 7)
$P^2m^{1/2}$	1.415 (E − 5)	1.089 (E − 5)	−3.14 (E − 6)	−3.11 (E − 6)	4.239 (E − 5)
$P^2tm^{1/2}$	0	0	0	0	2.261 (E − 7)
P^3	2.158 (E − 8)	6.50 (E − 9)	1.496 (E − 8)	9.82 (E − 9)	1.567 (E − 8)
$P^3m^{1/2}$	−8.11 (E − 9)	−6.26 (E − 9)	−5.3 (E − 11)	0	−1.662 (E − 8)
P^4	−6.48 (E − 12)	0	−6.54 (E − 12)	−3.08 (E − 12)	0
Std dev	0.23	0.08	0.18	0.24	0.28

[a] The terms (E − *a*), given for each variable, mean the coefficient is times 10^{-a}.

Table V. Coefficients for Equation 3[a]

Variables	NaCl	KCl	$MgCl_2$	Na_2SO_4	$MgSO_4$
$\phi_V{}^0{}_{,1\,atm}$ 0 °C	12.90	23.63	10.42	2.33	−13.06
t	0.1990	0.1788	0.2660	0.508	0.3720
t^2	−2.008 (E − 3)	−2.000 (E − 3)	−4.128 (E − 3)	−5.456 (E − 3)	−5.472 (E − 3)
$m^{1/2}$	1.5992	1.407	8.132	8.188	33.3710
$tm^{1/2}$	5.388 (E − 3)	1.118 (E − 2)	−0.0498	0.1777	−0.2963
$t^2m^{1/2}$	2.194 (E − 4)	1.848 (E − 4)	1.277 (E − 3)	−1.8704 (E − 3)	1.314 (E − 2)
m	1.004	1.235	−0.820	13.427	−40.4948
tm	−4.951 (E − 2)	−5.714 (E − 2)	−0.2202	−0.7505	−4.843 (E − 2)
t^2m	3.082 (E − 4)	5.256 (E − 4)	3.382 (E − 3)	9.2568 (E − 3)	−2.821 (E − 2)
$m^{3/2}$	0	0	0	0	28.8998
$tm^{3/2}$	0	0	0	0	0.2388
$t^2m^{3/2}$	0	0	0	0	2.482 (E − 2)
Av dev	0.05_1	0.01_0	0.03_3	0.04_1	0.02_8

[a] The terms (E − *a*), given for each variable, mean the coefficient is times 10^{-a}.

$$\phi_V{}^0(0) = \sum_i^n \phi_i t^i \tag{3a}$$

$$A = \sum_i^n A_i t^i \tag{3b}$$

$$B = \sum_i^n B_i t^i \tag{3c}$$

$$C = \sum_i^n C_i t^i \tag{3d}$$

The coefficients for eq 3 are given in Table V along with the standard deviations.

The temperature effect on the apparent molal volumes at 1000 bars and $I_m = 1$ is shown in Figure 5. The values of ϕ_V for NaCl and KCl increase with temperature, the values of ϕ_V for $MgCl_2$ have small temperature effects, while ϕ_V's for Na_2SO_4 increase rapidly at temperatures between 0 and 30 °C, then start to level off and have a tendency to decrease at temperatures above 40 °C. The values of ϕ_V for $MgSO_4$ actually show a maximum at 30 °C.

The smoothed apparent molal volumes of these electrolytes calculated from eq 2 and 3 can be used to calculate the densities by using the equation

$$d = d^0(1000 + mM)/(d^0 m\phi_V + 1000) \tag{4}$$

The average errors in ϕ_V for NaCl at 1000 bars are approximately ±0.1 (at $I_m = 1.0$) and ±0.2 (at $I_m = 0.1$) $cm^3\ mol^{-1}$, which correspond to density errors of ±100 and ±20 g cm^{-3}, respectively. The density errors for other salts are smaller.

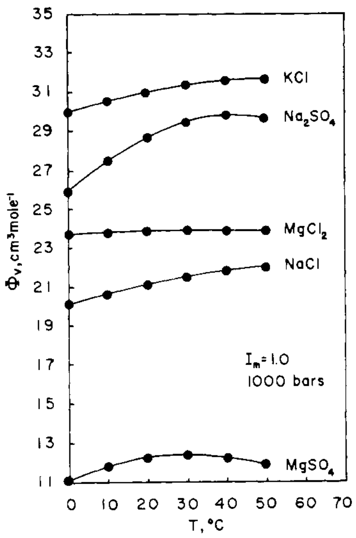

Figure 5. Apparent molal volumes of NaCl, KCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ as functions of temperature at $I_m = 1$ and 1000 bars.

The apparent molal compressibilities can be calculated by differentiating eq 1 with respect to pressure

$$\phi_K = -\partial\phi_V/\partial P \tag{5}$$

The values of ϕ_K for NaCl, $MgCl_2$, and Na_2SO_4 calculated at I_m = 1.0, 0 °C, and 1 atm agree reasonably with the data of Millero

Table VI. Comparisons of ϕ_K Obtained in this Study and the Data of Millero et al. at I_m = 1.0, 0 °C, and 1 Atm

Salt	$-10^4\phi_K$ (ours)	$-10^4\phi_K{}^a$ (Millero et al.)
NaCl	78 ± 28	60.4
$MgCl_2$	143 ± 22	121.2
Na_2SO_4	219 ± 29	171.4
$MgSO_4$	213 ± 24	156.4

[a] Millero et al. (*16*), eq 10.

et al. (*16*) (Table VI). The result of $MgSO_4$ is higher than the data of Millero et al.

Currently, the atmospherical densities and heat capacities of the major sea salts are being measured over a wide temperature range in our laboratory. Also the high pressure sound speed in the aqueous solutions of the major sea salts is being measured; these new results will be combined with the atmospherical densities and heat capacities to give precise equations of state for the major sea salts. The apparent molal volumes and compressibilities calculated from the sound-derived equations of state will be compared with the results of this study.

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Preliminary Data on the Pressure Effect on the Viscosity of Sodium Chloride–Water Solutions in the Range 10–40 °C

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The paper describes new, and preliminary, measurements of the viscosity of NaCl solutions in H_2O over a range of temperatures 10–40 °C, a range of pressures 0–30.0 MPa, and at three concentrations, together with check measurements on pure water. The precision is 0.2% and the accuracy is 0.3%. The measurements are represented by a purely empirical, analytic correlation which reproduces the ensemble of data with a standard deviation of 0.2%.

In conjunction with the expanding national program of research and development in geothermal energy, White and Williams (*27*), ERDA (*2*), it becomes increasingly more important to have access to a variety of thermophysical data concerning brines. In this connection the viscosity plays an important role, because it is needed to calculate pressure losses in wells, ducts, and channels, and, even more importantly, it is essential for the determination of porosities of rocks. Finally, the possibility that Walden's rule, Erdey-Grúz (*3*), may be applicable, opens the prospect of replacing the measurement of equivalent electric conductance by the, usually simpler, measurement of viscosity.

In order to make a contribution to the solution of this problem, we have organized a program of measurement of the viscosity of a number of brines as a function of pressure, temperature, and composition. The measurements are performed in a slightly modified oscillating-disk viscometer, Kestin and Moszynski (*13*) and Kestin and Leidenfrost (*10*), which has been successfully used in the past for the determination of the viscosity of compressed water, Moszynski (*19*), as well as superheated steam, Kestin and Wang (*16*) and Kestin and Richardson (*14*).

It is natural that a program of measurements on a variety of ionic solutions should start with solutions of sodium chloride. The present paper contains a very preliminary account of our results in the range of temperatures 10–40 °C, in the pressure range 0–30.0 MPa (MPa = $10^6 N/m^2$ = 10 bar = 145.04 psi), and over a range of compositions up to about 90% of saturation.

The viscosity of sodium chloride solutions has been measured by a number of investigators, notably by Kaminsky (*5*). Suryanarayana and Venkatesan (*24*), Korosi and Fabuss (*17*), Lengyel (*18*), Ostroff, Snowden, and Woessner (*20*), and Werblan, Rotowska, and Minc (*26*). Data are also listed in the book by Stokes and Mills (*23*). The measurements available in the literature cover the full range of compositions and a range of temperatures up to 150 °C; they all seem to have been performed by the capillary-flow method, and almost exclusively with the aid of an Ubbelohde-Rankine type of viscometer. However, as far as pressures are concerned, we were unable to locate any measurements at pressures higher than about 1.4 MPa, Potter, Shaw, and Haas (*21*). The fact that ours seem to be the first measurements which throw light on the effect of pressure on the viscosity of concentrated ionic solutions has provided the motivation for the preparation of this preliminary account. A more detailed report is reserved for a future date.

2. The Method

The data on the viscosity of NaCl–H_2O solutions described in this paper have been obtained in an oscillating-disk instrument.