Journal of chemical & engineering data

pubs.acs.org/jced

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Molar Volumes and Heat Capacities of Aqueous Solutions of $Mg(ClO_4)_2$

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Cite This: https://dx.doi.org/10.1021/acs.jced.0c00358

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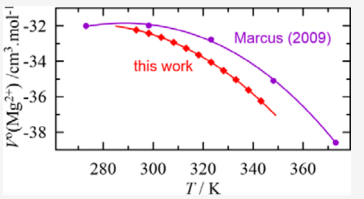
ABSTRACT: Densities and isobaric heat capacities of about 25 aqueous solutions of magnesium perchlorate, $Mg(ClO_4)_2(aq)$, have been measured at concentrations $0.01 \lesssim m/\text{mol·kg}^{-1} \lesssim 2.5$ using vibrating tube densimetry and flow calorimetry, respectively. Densities were determined at temperatures from 293.15 to 343.15 at 5 K intervals, but heat capacities were restricted to 298.15 K. These data were used to calculate the corresponding apparent molar volumes, V_ϕ, and isobaric heat capacities, $C_{p\phi}$, which were extrapolated to infinite dilution using appropriate semi-empirical equations to give the standard-state values, V° and C_p°. Where comparisons were possible, the present results are in good agreement with literature data but are more extensive and precise. Standard values for $Mg^{2+}(aq)$ were obtained using appropriate extrathermodynamic assumptions and also agreed well with literature estimates. Unlike many inorganic salts, the V° values for $Mg(ClO_4)_2(aq)$ do not show a maximum over the investigated temperature range.



1. INTRODUCTION

The aqueous solutions of magnesium perchlorate, $Mg(ClO_4)_2(aq)$, have attracted considerable interest, for example, as battery electrolytes because of their relatively high electrical conductivity.[1−3] Reflecting the very strong hydration of the magnesium ion, aqueous solutions of $Mg(ClO_4)_2$ also find application in controlling relative humidity in various environments.[4] Indeed, the detection of $Mg(ClO_4)_2(aq)$ in the Martian environment has led to a lively commentary about the possible presence of liquid water on that planet.[5] Anhydrous $Mg(ClO_4)_2$ is also a powerful siccative for drying gases.[4] In organic chemistry, $Mg(ClO_4)_2$ is an effective agent for the promotion of acylation, acetylation, and esterification and has been used as a catalyst for polymerization and hydrolysis reactions.[6,7]

Heat capacities and densities of aqueous electrolyte solutions are essential quantities for the heat and mass transfer calculations used in process engineering.[8] They also provide useful insights into the nature of ion−ion and ion−solvent interactions in solution.[9,10] Reliable values of these two properties are especially important for aqueous solutions of $Mg(ClO_4)_2$ because this salt is one of the few Mg^{2+}-containing electrolytes that can be regarded as essentially fully dissociated at reasonable concentrations.[10,11] Such a characteristic is critical for the accurate estimation of standard-state (infinite dilution) values for the salt itself and for $Mg^{2+}(aq)$.[11−14] This is because it is difficult to reliably extrapolate volumetric or heat capacity data to zero concentration, even for modestly associated salts, because of the formation of ion pairs. The often-unsuspected presence of such species can significantly affect the observed properties of electrolyte solutions.[10,11,15]

Densities of $Mg(ClO_4)_2(aq)$ have been reported over a limited temperature range in several publications. Thus, Lumme[16] used pycnometry to determine densities of a number of perchlorate salts, including $Mg(ClO_4)_2$, at three temperatures (293.15, 298.15, and 303.15 K) over the concentration range $0.001 \leq c/\text{mol·L}^{-1} \leq 2$. Latysheva and Andreeva[17] also used pycnometry, at the same three temperatures, to measure densities for various divalent perchlorate salts at five concentrations in the range $0.1 \leq m/\text{mol·kg}^{-1} \leq 4$. The only other data available were obtained at 298.15 K. Thus, Spitzer et al.[18] employed vibrating tube densimetry (vtd) to measure densities of 13 solutions of $Mg(ClO_4)_2(aq)$ over a limited concentration range, $0.037 \leq m/\text{mol·kg}^{-1} \leq 0.26$. Kiselev and co-workers[19,20] reported densities at five concentrations over the range $0.02 \leq m/\text{mol·kg}^{-1} \leq 0.2$ also using vtd. These data will be further discussed in relation to the present results in Section 3.3 below.

A limited number of studies of isobaric heat capacities of $Mg(ClO_4)_2(aq)$ have also been reported. Latysheva and Andreeva[21] employed a conventional static calorimeter to determine apparent molar heat capacities, $C_{p\phi}$, for six solutions at 298.15 K over the concentration range $0.1 \leq m/\text{mol·kg}^{-1} \leq 4$. Spitzer et al.[18] reported $C_{p\phi}$ values, also at 298.15 K, using Picker flow calorimetry, under the conditions described above.

Received: April 20, 2020
Accepted: June 4, 2020

Table 1. Sample Sources and Purities

chemical name	CASRN	source	mass fraction purity	purification method	analysis method
magnesium oxide	1309-48-4	Ajax Chemicals	≥0.99	see text	none
perchloric acid	7601-90-3	Ajax Chemicals	0.70[a]	none	none
magnesium perchlorate	10034-81-8	synthesis	0.995	filtration	evaporative gravimetry

[a]This figure is the $HClO_4$ content; other impurities were stated to be <0.01 mass % in total.

More recently, Toner and Catling[5] used differential scanning calorimetry to determine heat capacities of nine solutions, at $0.50 \leq m/\text{mol·kg}^{-1} \leq 4.25$, over the unusually wide temperature range (at least for some solutions) of $298.15 \leq T/\text{K} \leq 178.15$. These results are further discussed in Section 3.5 below.

The present paper reports densities and heat capacities of ca. 25 aqueous solutions of $Mg(ClO_4)_2$ over the concentration range $0.01 \lesssim m/\text{mol·kg}^{-1} \lesssim 2.5$. Densities were measured at temperatures $293.15 \leq T/\text{K} \leq 343.15$ by vtd while isobaric volumetric heat capacities were obtained by Picker flow calorimetry at 298.15 K only. These quantities were used to calculate the corresponding apparent molar properties, V_ϕ and $C_{p\phi}$. Particular attention was paid to measurements at low concentrations so as to optimize evaluation of the standard-state (infinite dilution) values for $Mg(ClO_4)_2(aq)$ and, via appropriate extrathermodynamic assumptions,[10,22] the corresponding values for the important $Mg^{2+}(aq)$ ion.

2. EXPERIMENTAL SECTION

2.1. Reagents. Details of the sources and purities of the chemicals used in this work are summarized in Table 1. However, because solute purity is critical for high-accuracy measurements,[22] some further details are appropriate. Briefly, solid MgO (~100 g) was boiled with high-purity water (2.5 L) for 1 h and collected by vacuum filtration (Millipore, 0.45 μm). The wet solid was then twice slurried with cold water and filtered. MgO(s) so obtained was dissolved in analytical-grade $HClO_4$ to give a concentrated (~2.5 mol·kg^{-1}) solution of $Mg(ClO_4)_2(aq)$ with pH ≈ 6.5. The stock solution was filtered and analyzed by evaporative gravimetry, initially at 150 °C to remove bulk water and then at 200 °C in a vacuum oven. Triplicate results agreed within ±0.02 mass %. More dilute solutions were prepared by weight. High-purity water (Ibis Technology, Australia) and buoyancy corrections were used throughout.

2.2. Density Measurements. Densities were measured at temperatures $293.15 \leq T/\text{K} \leq 343.15$ in 5 K intervals, at atmospheric pressure, using vtd (Anton Paar, Austria, Model DMA 5000 M) over the concentration range $0.01 \lesssim m/\text{mol·kg}^{-1} \lesssim 2.5$. Measurements were made using the protocol described in detail previously.[23] Briefly, the densimeter was calibrated with water and air following the manufacturer's protocol. Solution densities were determined isoplethically using both increasing and decreasing temperature scans over the targeted range. Agreement between the upward and downward scans was routinely within 3 $\mu\text{g·cm}^{-3}$. Each sample scan was bracketed by equivalent temperature scans of pure water, which also normally agreed to within 3 $\mu\text{g·cm}^{-3}$. As usual,[22,23] agreement between replicate determinations of the salt solutions decreased with increasing solute concentration but was typically ca. 3 to 10 $\mu\text{g·cm}^{-3}$.

2.3. Heat Capacity Measurements. Isobaric volumetric heat capacities (σ_p) of the solutions were measured using a Picker flow calorimeter (Sodev, Sherbrooke, Canada, model CP-Cpr) following the procedure described elsewhere.[24] The temperature was controlled to ±2 mK with a circulator thermostat (Sodev, model CT-L). The fluid flow rate was maintained at 0.7 mL·min^{-1} using a peristaltic pump (Gilson, Minipulse, USA). The σ_p values reported are the averages of the first and second "leg" measurements[24] at each concentration. No significant differences between the two "legs" were observed for the present solutions, even at high solute concentrations.

3. RESULTS AND DISCUSSION

3.1. Densities. Measured density differences ($\Delta\rho$) at the desired temperature

$$\Delta\rho = \rho - \rho_w \tag{1}$$

where ρ_w and ρ are the densities of pure water and the target solution, respectively, as summarized in Table 2. The ρ_w values were calculated using the International Association of the Properties of Water and Steam IAPWS-95 formulation.[25] For convenience, these values are also listed in Table 2 and can be used to calculate solution densities via eq 1.

3.2. Molar Volumes. Apparent molar volumes, V_ϕ, for $Mg(ClO_4)_2(aq)$ are listed in Table 2 and were obtained from the experimental density data via the usual equation

$$V_\phi = \frac{M_s}{\rho} - \frac{\Delta\rho}{m\cdot\rho_w\cdot\rho} \tag{2}$$

where m is the solute concentration. The molar mass, M_s, for $Mg(ClO_4)_2$ was calculated to be 0.22321 kg·mol^{-1} using IUPAC 2017 Atomic Weights of the Elements.[26]

The temperature and concentration dependences of V_ϕ (Figure 1) were fitted for convenience using a Pitzer-type equation[10,22]

$$V_\phi = \omega A_V \ln(1 + b\sqrt{m})/b + \sum_i a_i\cdot\varphi_i(m, T) \tag{3}$$

where A_V is the temperature-dependent Debye–Hückel theoretical slope for volumes, $\omega = [(\nu_+ + \nu_-)\cdot z_+\cdot z_-/2]^{1.5}$ is a valence factor that has the value of 5.196 for $Mg(ClO_4)_2$, and b is a constant having the value 2.8 $\text{kg}^{0.5}\text{·mol}^{-0.5}$. Values of A_V were obtained from the literature as described previously.[23] The quantities a_i are empirical adjustable parameters obtained by fitting the observed data with eq 3 while $\varphi_i(m,T)$ values are basis functions of molality and temperature.[23] Extrapolation of eq 3 to zero molality yields the apparent molar volume of the solute at infinite dilution, V°, ($=\overline{V}_2^\circ$, its standard partial molar volume). For convenience, the values of A_V and V° are listed as functions of temperature in Table 3 while the fitting functions (including the adjustable parameters) are recorded in Table 4, noting that $\tau = T/1000$. The ability of eq 3 to fit the data over the investigated ranges of molality and temperature is illustrated by the deviation plot in the upper panel of Figure 1. As is usual, the deviations between the experimental and

https://dx.doi.org/10.1021/acs.jced.0c00358
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Table 2. Experimental Density Differences, $\Delta\rho$, and Apparent Molar Volumes, V_ϕ, for $Mg(ClO_4)_2(aq)$ as a Function of Molality, m, at Temperatures $293.15 \le T/K \le 343.15$ and Pressure $p = 0.1$ MPa[a]

m/mol·kg^{-1}	$\Delta\rho$/kg·m^{-3}	V_ϕ/cm^3·mol^{-1}	$\Delta\rho$/kg·m^{-3}	V_ϕ/cm^3·mol^{-1}	$U_c(V_\phi)$[b]/cm^3·mol^{-1}
	T = 293.15 K, ρ_w = 998.207 kg·m^{-3}		T = 298.15 K, ρ_w = 997.048 kg·m^{-3}		
0.010091	1.581	66.26	1.565	67.75	0.24
0.015481	2.422	66.43	2.398	67.89	0.18
0.020189	3.157	66.46	3.126	67.90	0.15
0.025452	3.977	66.53	3.933	68.16	0.13
0.030517	4.765	66.59	4.717	68.06	0.12
0.035239	5.493	66.80	5.437	68.29	0.12
0.040935	6.379	66.79	6.313	68.30	0.11
0.046467	7.240	66.75	7.163	68.31	0.11
0.050836	7.908	66.96	7.826	68.47	0.10
0.059940	9.315	67.02	9.221	68.48	0.10
0.059940	9.315	67.02	9.221	68.48	0.10
0.070321	10.918	67.06	10.801	68.62	0.10
0.084004	13.027	67.10	12.894	68.58	0.09
0.10285	15.917	67.22	15.755	68.69	0.09
0.12580	19.415	67.41	19.214	68.90	0.09
0.15114	23.271	67.51	23.028	69.01	0.09
0.20318	31.109	67.83	30.786	69.31	0.08
0.24551	37.414	68.12	37.033	69.55	0.08
0.30299	45.913	68.38	45.448	69.80	0.08
0.40451	60.728	68.76	60.110	70.16	0.08
0.49157	73.179	69.13	72.451	70.48	0.08
0.60886	89.669	69.55	88.786	70.87	0.07
0.81429	117.728	70.23	116.600	71.47	0.07
1.0069	143.087	70.84	141.756	72.01	0.07
1.4946	203.605	72.17	201.857	73.19	0.06
2.0035	261.190	73.53	259.133	74.42	0.06
2.5085	313.603	74.68	311.325	75.46	0.05
	T = 303.15 K, ρ_w = 995.649 kg·m^{-3}		T = 308.15 K, ρ_w = 994.033 kg·m^{-3}		
0.010091	1.551	69.03	1.538	70.19	0.24
0.015481	2.375	69.26	2.355	70.43	0.18
0.020189	3.097	69.22	3.072	70.33	0.15
0.025452	3.897	69.46	3.865	70.59	0.13
0.030517	4.672	69.42	4.633	70.57	0.12
0.035239	5.387	69.60	5.343	70.72	0.12
0.040935	6.254	69.63	6.201	70.80	0.11
0.046467	7.095	69.66	7.035	70.82	0.11
0.050836	7.754	69.77	7.690	70.91	0.10
0.059940	9.136	69.78	9.060	70.92	0.10
0.059940	9.136	69.78	9.060	70.92	0.10
0.070321	10.701	69.92	10.611	71.08	0.10
0.084004	12.775	69.88	12.667	71.03	0.09
0.10285	15.608	70.00	15.476	71.16	0.09
0.12580	19.034	70.21	18.873	71.36	0.09
0.15114	22.810	70.33	22.617	71.48	0.09
0.20318	30.497	70.61	30.239	71.74	0.08
0.24551	36.689	70.83	36.380	71.95	0.08
0.30299	45.028	71.05	44.649	72.17	0.08
0.40451	59.556	71.39	59.059	72.48	0.08
0.49157	71.794	71.68	71.199	72.75	0.08
0.60886	87.990	72.03	87.271	73.07	0.07
0.81429	115.581	72.57	114.659	73.56	0.07
1.0069	140.550	73.06	139.456	74.00	0.07
1.4946	200.264	74.11	198.812	74.94	0.06
2.0035	257.252	75.22	255.530	75.95	0.06
2.5085	309.240	76.17	307.331	76.81	0.05
	T = 313.15 K, ρ_w = 992.216 kg·m^{-3}		T = 318.15 K, ρ_w = 990.213 kg·m^{-3}		
0.010091	1.526	71.24	1.516	72.08	0.24
0.015481	2.337	71.45	2.321	72.34	0.18
0.020189	3.048	71.39	3.027	72.28	0.15

https://dx.doi.org/10.1021/acs.jced.0c00358
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Table 2. continued

m/mol·kg^{-1}	$\Delta\rho$/kg·m^{-3}	V_ϕ/cm^3·mol^{-1}	$\Delta\rho$/kg·m^{-3}	V_ϕ/cm^3·mol^{-1}	$U_c(V_\phi)^b$/cm^3·mol^{-1}
0.025452	3.838	71.51	3.813	72.35	0.13
0.030517	4.599	71.55	4.568	72.42	0.12
0.035239	5.303	71.72	5.267	72.59	0.12
0.040935	6.155	71.78	6.113	72.66	0.11
0.046467	6.982	71.83	6.935	72.69	0.11
0.050836	7.633	71.89	7.582	72.75	0.10
0.059940	8.992	71.93	8.930	72.81	0.10
0.059940	8.992	71.93	8.930	72.81	0.10
0.070321	10.530	72.09	10.458	72.97	0.10
0.084004	12.571	72.04	12.484	72.93	0.09
0.10285	15.357	72.18	15.250	73.07	0.09
0.12580	18.728	72.37	18.598	73.26	0.09
0.15114	22.445	72.48	22.290	73.36	0.09
0.20318	30.007	72.75	29.798	73.63	0.08
0.24551	36.101	72.94	35.849	73.82	0.08
0.30299	44.306	73.16	43.997	74.03	0.08
0.40451	58.610	73.44	58.204	74.30	0.08
0.49157	70.660	73.70	70.173	74.54	0.08
0.60886	86.620	73.99	86.030	74.81	0.07
0.81429	113.823	74.43	113.063	75.22	0.07
1.0069	138.462	74.84	137.558	75.59	0.07
1.4946	197.487	75.68	196.277	76.35	0.06
2.0035	253.956	76.60	252.516	77.19	0.06
2.5085	305.583	77.39	303.984	77.91	0.05
	T = 323.15 K, ρ_w = 988.035 kg·m^{-3}		T = 328.15 K, ρ_w = 985.693 kg·m^{-3}		
0.010091	1.507	72.82	1.500	73.34	0.25
0.015481	2.308	73.02	2.296	73.63	0.18
0.020189	3.008	73.06	2.992	73.69	0.15
0.025452	3.790	73.09	3.769	73.75	0.13
0.030517	4.540	73.18	4.515	73.83	0.12
0.035239	5.235	73.34	5.205	74.03	0.12
0.040935	6.076	73.41	6.043	74.05	0.11
0.046467	6.894	73.42	6.857	74.05	0.11
0.050836	7.536	73.49	7.495	74.14	0.10
0.059940	8.874	73.59	8.824	74.26	0.10
0.059940	8.874	73.59	8.824	74.26	0.10
0.070321	10.395	73.71	10.339	74.34	0.10
0.084004	12.406	73.70	12.336	74.37	0.09
0.10285	15.153	73.86	15.066	74.54	0.09
0.12580	18.480	74.04	18.374	74.72	0.09
0.15114	22.150	74.13	22.024	74.80	0.09
0.20318	29.610	74.40	29.439	75.08	0.08
0.24551	35.620	74.60	35.414	75.28	0.08
0.30299	43.717	74.80	43.464	75.47	0.08
0.40451	57.837	75.05	57.504	75.71	0.08
0.49157	69.731	75.28	69.330	75.94	0.08
0.60886	85.494	75.53	85.008	76.17	0.07
0.81429	112.372	75.91	111.744	76.53	0.07
1.0069	136.735	76.25	135.985	76.84	0.07
1.4946	195.173	76.94	194.166	77.47	0.06
2.0035	251.201	77.71	250.001	78.19	0.06
2.5085	302.522	78.37	301.188	78.79	0.05
	T = 333.15 K, ρ_w = 983.196 kg·m^{-3}		T = 338.15 K, ρ_w = 980.551 kg·m^{-3}		
0.010091	1.493	73.85	1.487	74.26	0.25
0.015481	2.287	74.03	2.278	74.42	0.18
0.020189	2.977	74.26	2.964	74.71	0.15
0.025452	3.749	74.36	3.733	74.80	0.14
0.030517	4.493	74.38	4.473	74.85	0.12
0.035239	5.180	74.56	5.158	75.00	0.12
0.040935	6.013	74.61	5.986	75.08	0.11
0.046467	6.824	74.58	6.794	75.04	0.11

https://dx.doi.org/10.1021/acs.jced.0c00358
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Table 2. continued

m/mol·kg^{-1}	$\Delta\rho$/kg·m^{-3}	V_ϕ/cm^3·mol^{-1}	$\Delta\rho$/kg·m^{-3}	V_ϕ/cm^3·mol^{-1}	$U_c(V_\phi)$[b]/cm^3·mol^{-1}
0.050836	7.458	74.69	7.425	75.15	0.10
0.059940	8.779	74.84	8.739	75.32	0.10
0.059940	8.779	74.84	8.739	75.32	0.10
0.070321	10.288	74.89	10.243	75.35	0.10
0.084004	12.273	74.95	12.218	75.42	0.09
0.10285	14.987	75.14	14.917	75.64	0.09
0.12580	18.280	75.30	18.195	75.80	0.09
0.15114	21.911	75.38	21.810	75.87	0.09
0.20318	29.285	75.67	29.147	76.17	0.08
0.24551	35.229	75.87	35.062	76.37	0.08
0.30299	43.235	76.06	43.030	76.56	0.08
0.40451	57.202	76.30	56.930	76.80	0.08
0.49157	68.968	76.51	68.641	77.01	0.08
0.60886	84.568	76.74	84.171	77.22	0.07
0.81429	111.175	77.07	110.660	77.54	0.07
1.0069	135.304	77.37	134.687	77.82	0.07
1.4946	193.250	77.94	192.418	78.36	0.06
2.0035	248.908	78.60	247.917	78.97	0.06
2.5085	299.973	79.16	298.872	79.49	0.05
	T = 343.15 K, ρ_w = 977.650 kg·m^{-3}				
0.010091	1.481	74.65			0.25
0.015481	2.269	74.80			0.18
0.020189	2.953	75.06			0.15
0.025452	3.720	75.12			0.14
0.030517	4.455	75.24			0.12
0.035239	5.139	75.35			0.12
0.040935	5.962	75.48			0.11
0.046467	6.767	75.43			0.11
0.050836	7.396	75.53			0.10
0.059940	8.704	75.71			0.10
0.059940	8.704	75.71			0.10
0.070321	10.202	75.74			0.10
0.084004	12.169	75.81			0.09
0.10285	14.854	76.06			0.09
0.12580	18.120	76.21			0.09
0.15114	21.720	76.27			0.09
0.20318	29.024	76.59			0.08
0.24551	34.914	76.79			0.08
0.30299	42.846	76.99			0.08
0.40451	56.688	77.22			0.08
0.49157	68.348	77.43			0.08
0.60886	83.816	77.63			0.07
0.81429	110.199	77.94			0.07
1.0069	134.132	78.21			0.07
1.4946	191.667	78.71			0.06
2.0035	247.022	79.28			0.06
2.5085	297.881	79.77			0.05

[a]Standard uncertainties: $u(T)$ = 0.002 K, $u_r(m)$ = 0.0005, $u(p)$ = 1 kPa, and $u(\Delta\rho/\text{kg·m}^{-3})$ = 0.002 + 0.0002($\Delta\rho$/kg·m^{-3}). [b]Combined uncertainty, common to both V_ϕ values in the same row.

calculated V_ϕ values increase with decreasing m, as $(\rho - \rho_w) \rightarrow 0$ (cf. eq 2).[10,22]

At 298.15 K, the present value of V° = 67.09 cm^3·mol^{-1} (Table 3) is in near-quantitative agreement with the sum (67.07 cm^3·mol^{-1}) of the ionic volumes listed[12−14] for Mg^{2+}(aq) and ClO_4^-(aq), although it should be noted that both these values almost certainly have much larger real uncertainties than this agreement indicates.[12,27] At higher temperatures, where the literature data are not so well characterized, the agreement is less satisfactory with differences of up to 2.6 cm^3·mol^{-1}. The present results are probably more reliable, not least because Millero's V° values at T > 298 K[12,13] adopted by Marcus[14] were apparently obtained via the empirical Masson equation, which can easily introduce errors of this magnitude.[12,22]

The variations of V° and V_ϕ with temperature are shown in Figure 2. Regardless of composition, all the plots are decidedly nonlinear. This indicates that (at least for this salt) the apparent molar expansibilities E_ϕ $(=\partial V_\phi/\partial T)$ are not, as is often assumed for electrolyte solutions,[10,12] independent of

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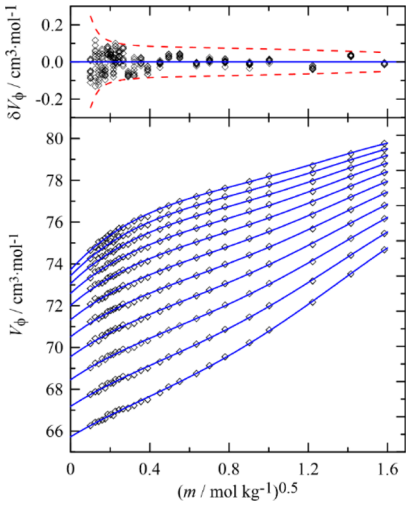

Figure 1. Lower box: Apparent molar volumes, V_ϕ, of $Mg(ClO_4)_2$(aq) as a function of concentration ($\sqrt{m}$) at various temperatures (bottom to top): T/K = 293.15, 298.15, 303.15, 308.15, 313.15, 318.15, 323.15, 328.15, 333.15, 338.15, 343.15. Lines were calculated from eq 3 using the parameters in Table 4. Upper box: deviations, δV_ϕ = V_ϕ(obs) − V_ϕ(fit), of observed apparent molar volumes from fitted values. Red dashed lines represent the experimental uncertainty, $U_c(V_\phi)$.

Table 3. Temperature Dependence of the Volumetric Debye−Hückel Limiting Slope (A_V) and Standard Molar Volumes ($V°$) for $Mg(ClO_4)_2$(aq) at Pressure p = 0.1 MPa

T/K	A_V/cm³·kg^0.5·mol^−1.5	$V°$/cm³·mol^−1[a]
293.15	1.8219	65.63
298.15	1.8979	67.09
303.15	1.9799	68.36
308.15	2.0685	69.46
313.5	2.1639	70.41
318.5	2.2666	71.22
323.15	2.3768	71.91
328.15	2.4951	72.48
333.15	2.6219	72.94
338.15	2.7576	73.31
343.15	2.9028	73.60

[a]Combined uncertainty $U_c(V°)$ = 0.08 cm³·mol^−1 at all temperatures.

Table 4. Basis Functions, φ_i, and Fitting Parameters, a_i, of Eq 3 for V_ϕ of $Mg(ClO_4)_2$(aq), Valid at 293.15 ≤ T/K ≤ 343.15 and p = 0.1 MPa

$\varphi_i(\tau,m)$	a_i	standard error	|t-statistic|
1	151.274	0.559	271
T	−171.444	1.40	122
$1/\tau^4$	−0.261307	0.00113	231
$\beta(m)$[a]	−0.583029	0.0176	33
m/τ^3	−0.49406	0.00642	77
m/τ^4	0.162541	0.00198	82
m^2/τ	−0.818202	0.0414	20
$m^2\tau$	11.9251	0.635	19
$m^2\tau^4$	−108.141	7.00	15

[a]$\beta(m) = 1 - e^{8.1406\sqrt{m}}\cdot(1 + 8.1406\sqrt{m})$

temperature, even over the present limited range. It is noteworthy that unlike most inorganic salts,[12−14] the present values of $V°$ and V_ϕ for $Mg(ClO_4)_2$(aq) do not exhibit a maximum over the studied temperature range, although they are clearly approaching one to T > 343 K (Figure 2).

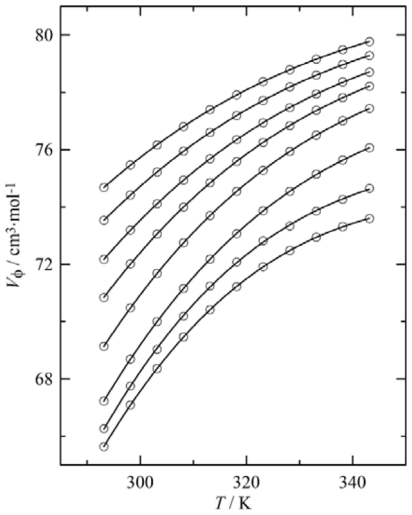

Figure 2. Temperature dependence of the apparent molar volume V_ϕ of $Mg(ClO_4)_2$(aq) at concentrations (bottom to top): m/mol·kg^−1 = 0, 0.01, 0.10, 0.49, 1.01, 1.50, 2.00, 2.50. Note that some values have been omitted for representational clarity. Lines are calculated from eq 3 using the parameters in Table 4.

3.3. Comparisons of V_ϕ with Literature Data. Figure 3 plots the present and literature[16−20] values of V_ϕ at 298.15 K.

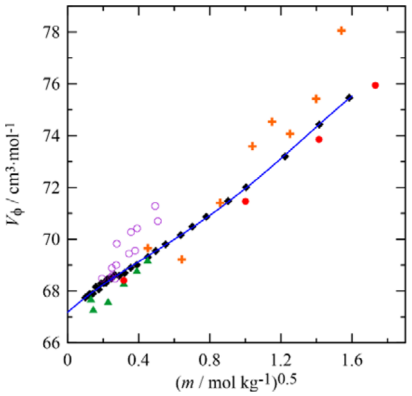

Figure 3. Comparison of present and literature values of V_ϕ for $Mg(ClO_4)_2$(aq) at 298.15 K: ◆ this work; green ▲ refs 19 and 20; purple ○ ref 18; red ● ref 17; orange + ref 16. Line is a fit of this work using eq 3. Note that the divergent values of Lumme[16] at c < 0.04 mol·L^−1 have been omitted for representational convenience (see text).

Similar results (not shown) are observed at other temperatures, albeit with fewer data. Overall, the agreement amongst independent determinations is reasonable, generally within 2 cm³·mol^−1. The major exceptions are the V_ϕ values at low concentrations derived from the density data of Lumme.[16] Note, however, that this author reported densities to only 4 decimal places and used solutions prepared on the less-precise mol·L^−1 scale. Accordingly, Lumme's V_ϕ values at c < 0.04 mol·L^−1, which differ from the present values by up to 11 cm³·mol^−1, are omitted from Figure 3. Another point to note is that while the V_ϕ values of Kiselev et al.[19,20] agree moderately well with the present results, with an average deviation of ±0.4 cm³·mol^−1 (Figure 3), they are algebraically inconsistent with their stated densities.

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3.4. Comparisons of V_ϕ of Selected Magnesium Salts.

Figure 4 compares the departures from Debye–Hückel behavior (dotted straight line) for aqueous solutions of $Mg(ClO_4)_2$, $MgCl_2$,[28] and $MgTf_2$[29] (Tf^- = triflate, $CF_3SO_3^-$). These salts were chosen because they are generally regarded as being largely dissociated.[30] The calculated departures (Figure 4) are systematically *negative*, in the order: $MgTf_2$ > $Mg(ClO_4)_2$ > $MgCl_2$ (least negative). As the volume changes for ion association reactions, ΔV_{assocn}, is generally *positive*, because of the decrease in electrostriction resulting from charge neutralization, and the plots in Figure 4 suggest the presence of (weak) association in the order: $MgTf_2$ < $Mg(ClO_4)_2$ < $MgCl_2$ (most associated). This is consistent with the binding tendencies of their anions, although other explanations are undoubtedly possible.

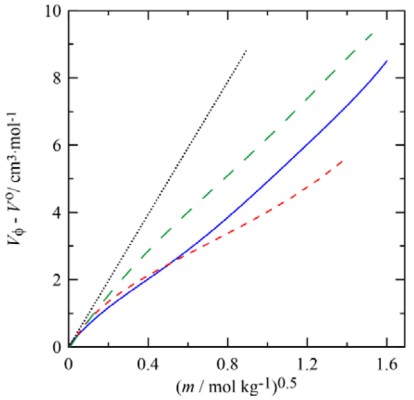

Figure 4. Differences ($V_\phi - V^\circ$) between apparent and standard molar volumes for some magnesium salts at 298.15 K: blue solid line, $Mg(ClO_4)_2$, this work; green long-dash line, $MgCl_2$;[28] red short-dash line, $MgTf_2$;[29] black dotted line, Debye–Hückel limiting slope.

3.5. Heat Capacities.

Isobaric volumetric heat capacities (σ_p/J·K^{-1}·cm^{-3}) obtained for $Mg(ClO_4)_2$(aq) at 298.15 K are summarized in Table 5, along with the corresponding massic heat capacity (c_p, also known as the specific heat capacity) and the apparent molar heat capacities ($C_{p\phi}$) derived from them. As the heat capacities were measured using the solutions employed for the density determinations, the required densities for calculating c_p ($=\sigma_p/\rho$) were derived from the relevant data in Table 2 via eq 1. Note that an extra significant figure has been included in the σ_p and c_p values listed in Table 5 to avoid round-off errors. Apparent molar heat capacities were obtained via the usual equation

$$C_{p\phi} = M_s c_p + (c_p - c_{pw}]/m \quad (4)$$

where c_{pw} is the isobaric massic heat capacity of pure water, with a value of 4181.3 J·K^{-1}·kg^{-1} taken from the IAPWS formulation,[25] and the other symbols at 298.15 K are as defined above.

The calculated $C_{p\phi}$ values are listed in Table 5 and are plotted along with literature data in Figure 5.

For convenience, the values of $C_{p\phi}(m)$ were fitted using an extended Redlich–Rosenfeld–Meyer-type equation, which had the form

$$C_{p\phi} = C_p^\circ + \omega A_C \sqrt{m} + B_C m + C_C m^{1.5} + D_C m^2 \quad (5)$$

where C_p° ($=\overline{C}_{p,2}^\circ$) is the standard-state (infinite dilution) partial molar isobaric heat capacity of the solute in the solvent. Of the other quantities in eq 5, ω is the valence factor defined above, A_C (= 31.766 J·K^{-1}·mol$^{-0.5}$·kg$^{0.5}$) is the currently accepted value of the Debye–Hückel theoretical slope for heat capacities at 298.15 K,[25] and Y_C (Y = B, C, D) values are empirical parameters derived from fitting the experimental data

Table 5. Experimental Isobaric Volumetric Heat Capacities σ_p, along with Massic c_p, Apparent Molar $C_{p\phi}$, and Heat Capacities for $Mg(ClO_4)_2$(aq) Solutions as a Function of Concentration m, at T = 298.15 K and p = 0.1 MPa[a]

m/mol·kg^{-1}	σ_p/J·K^{-1}·cm^{-3}	c_p/J·K^{-1}·g^{-1}	$C_{p\phi}$/J·K^{-1}·mol^{-1}	$U_c(C_{p\phi})$[b]/J·K^{-1}·mol^{-1}
0.01009	4.1656	4.1714	−49.2	4.2
0.01548	4.1639	4.1662	−46.6	3.7
0.02019	4.1624	4.1617	−41.7	3.5
0.04094	4.1560	4.1421	−34.1	3.2
0.04647	4.1542	4.1368	−34.6	3.2
0.05084	4.1530	4.1328	−31.8	3.1
0.05994	4.1500	4.1242	−32.4	3.1
0.07032	4.1468	4.1145	−32.1	3.0
0.08400	4.1425	4.1017	−31.7	3.0
0.1029	4.1371	4.0848	−26.5	3.0
0.1258	4.1301	4.0640	−25.4	2.9
0.1511	4.1226	4.0415	−22.7	2.9
0.2032	4.1079	3.9966	−16.7	2.8
0.2455	4.0957	3.9607	−14.3	2.8
0.3023	4.0802	3.9139	−9.0	2.8
0.4045	4.0526	3.8335	−4.1	2.7
0.6089	4.0018	3.6854	8.1	2.6
0.8143	3.9551	3.5514	19.1	2.5
1.007	3.9140	3.4369	27.8	2.4
1.495	3.8150	3.1822	41.9	2.2
2.004	3.7268	2.9667	56.0	2.1
2.509	3.6314	2.7755	59.1	1.9

[a]Standard uncertainties: $u(T)$ = 0.005 K, $u_r(m)$ = 0.0005, $u_r(\sigma_p)$ = 0.003, and $u_r(c_p)$ = 0.003. [b]Combined uncertainty.

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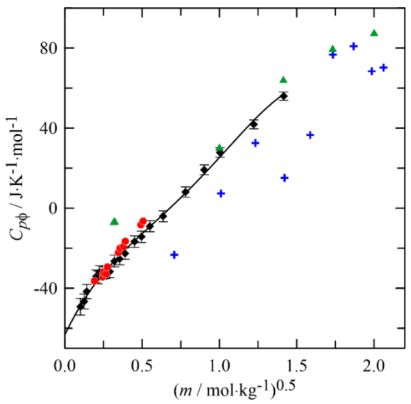

Figure 5. Comparison of present and literature values of $C_{p\phi}$ for $Mg(ClO_4)_2$(aq) at 298.15 K: ◆ this work; red ● ref 18; blue + ref 5; green ▲ ref 17. The line is a fit of the present data using eq 5.

to eq 5. The slight "waviness" in $C_{p\phi}(m)$ at higher concentrations ($m \gtrsim 0.3$ mol·kg^{-1}) is quite common for inorganic electrolytes[31−33] and is readily accommodated by eq 5.

The values obtained for the various parameters in eq 5 are recorded in Table 6. The present result of $C_p^\circ = -63 \pm 3$ J·K^{-1}·mol^{-1} for $Mg(ClO_4)_2$(aq) at 298.15 K is in excellent agreement with the experimental determination of −66 J·K^{-1}·mol^{-1} by Spitzer et al.[18] and with the summation of the relevant single-ion values reported by Hepler and Hovey (−68 J·K^{-1}·mol^{-1})[31] and by Marcus (−66 J·K^{-1}·mol^{-1}).[28] This level of agreement is particularly satisfying given that the uncertainties in C_p° are generally thought[28,32] to be of the order of 1−3 J·K^{-1}·mol^{-1}. Agreement of the present values with those of Latysheva and Andreeva[21] is reasonable except, as usual with static calorimeters,[33] at low m. Agreement with the data of Spitzer et al.[18] is excellent, with differences $\lesssim$5 J·K^{-1}·mol^{-1} throughout their limited concentration range (Figure 5). The scattered results of Toner and Catling[5] at 298.15 K, obtained by low-precision differential scanning calorimetry,[33] differ from the present values by up to 40 J·K^{-1}·mol^{-1} (Figure 5) and may be considered as, at best, rough approximations.[34,35]

Table 6. Parameters for Eq 5 Obtained by Fitting the $C_{p\phi}$ Data in Table 5 at 298.15 K and 0.1 MPa[a]

parameter	estimate	std. error	|t-statistic|
C_p°	−63.35	0.837	76
B_C	−211.51	10.4	20
C_C	198.59	15.4	13
D_C	−63.202	5.83	11

[a] ω = 5.1962, A_C = 31.766 J·K^{-1}·mol$^{-0.5}$·kg$^{0.5}$, $U_c(C_p^\circ)$ = 3 J·K·mol^{-1}.

3.6. Ionic Volumes and Heat Capacities. Although single-ion thermodynamic properties are not measurable, they are of considerable theoretical interest[10] and are required for the development of computer models of solution behavior.[36] Such quantities can be estimated by recourse to an appropriate "extrathermodynamic" assumption.[10] Current estimates of V° and C_p° for (ClO_4^-, aq)[14,27] are listed in Table 7. Values for Mg^{2+}(aq) were then calculated assuming ionic additivity (X = V or C_p)

$$X^\circ(Mg^{2+}, aq) = X^\circ(Mg(ClO_4)_2, aq) - 2X^\circ(ClO_4^-, aq) \quad (6)$$

Table 7. Standard Molar Volumes and Isobaric Heat Capacities for Mg^{2+}(aq)

T/K	$V^\circ(Mg(ClO_4)_2)$[a] (cm^3·mol^{-1})	$V^\circ(ClO_4^-)$[b] (cm^3·mol^{-1})	$V^\circ(Mg^{2+})$[c] (cm^3·mol^{-1})	$V^\circ(Mg^{2+})$[b] (cm^3·mol^{-1})
298.15	67.09	49.53	−31.97	−31.99
323.15	71.91	51.03	−30.15	−32.76
343.15	73.60	53.06[d]	−32.52	−34.5[d]
T/K	$C_p^\circ(Mg(ClO_4)_2)$[e] (J·K^{-1}·mol^{-1})	$C_p^\circ(ClO_4^-)$[f] (J·K^{-1}·mol^{-1})	$C_p^\circ(Mg^{2+})$[c] (J·K^{-1}·mol^{-1})	$C_p^\circ(Mg^{2+})$[f] (J·K^{-1}·mol^{-1})
298.15	−63.4	46	−155	−158

[a] Present work, Table 3. [b] Refs 14 and 27. [c] Present estimate using eq 6. [d] Interpolated from ref 14. [e] Present work, Table 6. [f] Ref 27.

Agreement of the present value of $V^\circ(Mg^{2+},aq)$ with Marcus's estimate,[14] which was based mainly on data for $MgCl_2$(aq), is quantitative at 298.15 K but only fair at higher T. Further high-quality investigations of a range of electrolyte solutions will be necessary to identify the source(s) of such differences. The corresponding data for heat capacities at 298.15 K are also presented in Table 7. Again, combination of the present results for $Mg(ClO_4)_2$(aq) with the recommended perchlorate value[27] gives via eq 6 a result for $C_p^\circ(Mg^{2+},aq)$ that is in exact agreement (within the likely error limits)[32] with Marcus's value.[27]

4. CONCLUSIONS

Reliable data for the densities (at 293.15 ≤ T/K ≤ 343.15) and isobaric heat capacities (at 298.15 K) have been determined for aqueous solutions of $Mg(ClO_4)_2$ over a wide concentration range. Special attention was given to the purity of the salt and to measurements at low solute concentrations. Apparent molar volumes (V_ϕ) and isobaric heat capacities ($C_{p\phi}$), calculated from the experimental data, increased smoothly with concentration and (for V_ϕ) temperature. At 298.15 K, agreement with literature values for V_ϕ and $C_{p\phi}$ is good, although differences increase at higher T. Unusually for simple inorganic salts, $V_\phi(T)$ for $Mg(ClO_4)_2$(aq) does not exhibit a maximum over the studied T range, although it is clearly approaching one to T > 343 K. Standard-state values, V° and C_p°, for $Mg(ClO_4)_2$ (aq) obtained by extrapolation of the present data to infinite dilution using semi-empirical equations are in quantitative agreement with literature results at 298.15 K but (for V°) differ somewhat at higher T. Similar results were obtained for the aquated magnesium ion, Mg^{2+}(aq), using established extrathermodynamic assumptions.

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https://dx.doi.org/10.1021/acs.jced.0c00358
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Funding

This work was funded by Murdoch University.

Notes

The authors declare no competing financial interest.

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