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Received for review February 14, 1974. Accepted June 4, 1974. Work supported by the National Science Foundation, Grant NSF-G14433.

Supplementary Material Available. Table I will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JCED-74-320.

Enthalpies of Dilution and Relative Apparent Molar Enthalpies of Aqueous Calcium and Manganous Perchlorates

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Enthalpies of dilution for $Ca(ClO_4)_2$ and $Mn(ClO_4)_2$ solutions were measured by solution calorimetry at 298.15K. Values of ϕ_L, the relative apparent molar enthalpy, were obtained over the range 0.003–7.7*m* for $Ca(ClO_4)_2$ and 0.008–4.2*m* for $Mn(ClO_4)_2$. A form of the Debye-Hückel equation guided reliable extrapolation to $m = 0$.

This paper is part of a series of investigations on the relative apparent molar enthalpy ϕ_L for 2-1 perchlorates. Values of ϕ_L for $Mg(ClO_4)_2$ and $Sr(ClO_4)_2$ were reported by Wood and Jongenburger (*17*) and for $Ba(ClO_4)_2$ by Vanderzee and Swanson (*14*). This work on $Ca(ClO_4)_2$ was undertaken to fill the gap in information for the above group of cations, for exploration of the effects of ion size and hydration on ϕ_L. The work on $Mn(ClO_4)_2$ is part of a related study on the first-row transition elements. Latysheva and Karavan (*2*) have measured enthalpies of dilution of saturated $Mn(ClO_4)_2$ solution and also the enthalpy of solution of $Mn(ClO_4)_2 \cdot 6H_2O(s)$ at 25°, 35°, and 45°C, but the results are not reduced to the reference state of infinite dilution. Values of ϕ_L derivable from their data, referred to the same reference state, agree well with ours, and from their data the standard enthalpy of solution of the hydrated salt can be calculated.

Experimental

Materials and analyses. A $Ca(ClO_4)_2$ stock solution was prepared by dissolving Mallinckrodt AR calcium carbonate (Lot XVX) in AR perchloric acid (60%). The resultant solution was slightly yellow; therefore, a small amount of charcoal was added, the solution was warmed and stirred, then cooled, and filtered to remove the charcoal and excess $CaCO_3$. The filtrate was warmed, concentrated by evaporation, and then enough distilled water added to give a solution near saturation at room temperature. A portion of this solution, diluted 1:100 with twice distilled water, had a pH of 4. The degree of acidity was ample to avoid possible thermal effects from hydrolysis (*6*) without making a significant contribution to ϕ_L for $Ca(ClO_4)_2$. The solution was analyzed with EDTA by recommended procedures (*15*), and other working solutions were prepared by mass dilution. Confirmatory analysis of a final solution from a calorimetric run supported the original assay. The initial stock solution was (7.686 ± 0.008)*m*, from three determinations.

$Mn(ClO_4)_2 \cdot 6H_2O$, G. F. Smith Co., was dissolved directly in twice distilled water to form an almost saturated solution at room temperature. A portion diluted 1:100 with twice distilled water had a pH of 4.4. At this level of acidity, hydrolytic effects should be negligible, and no significant thermal effects from excess acid should occur. The solution was analyzed with EDTA according to procedures by Welcher (*16*) and was (4.206 ± 0.005)*m* from three determinations. The assay was confirmed by potentiometric titration of a product solution from a calorimetric run with a standard permanganate solution (*18*). Other working solutions were prepared by mass dilution of the stock solution. The results of all weighings were reduced to mass, with densities from published tables for $Ca(ClO_4)_2$ (*5*) and $Mn(ClO_4)_2$ (*3*).

To suppress possible thermal effects from hydrolysis, dilutions were made into $10^{-4}m$ $HClO_4$ solutions prepared from twice distilled water. Thermal effects from this amount of background $HClO_4$ affect ϕ_L for the 2-1 electrolytes by less than 0.3 cal mol^{-1} and were not corrected for.

Calorimetric equipment and procedure. The calorimeter used in this investigation has been described elsewhere (*1, 10–14*). Temperatures were measured with a Hewlett-Packard HP-M40-2801A quartz thermometer, op-

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erated at a resolution of 10^{-5} K with minimum time between readings. Thermostat control was to ±0.0005K or better.

Dilution patterns and sample handling techniques were the same as those described elsewhere (*1, 10*) for similar studies in this laboratory.

All computations were performed by digital computer at the University of Nebraska Computing Center. Fore- and after-periods for the reactions were fitted by linear least squares, and corrected temperature changes were obtained by Dickinson's method.

Treatment of experimental data. The experimental data were treated as described previously (*1, 10*). The experimental ϕ_L values were fitted to the Debye-Hückel function used for similar studies in this laboratory (*1, 10, 14*). Table I lists the parameters of the equation, along with the range of molality fitted and the standard deviation σ. The ion-size parameter a was determined separately from activity coefficients for the two perchlorates (*4, 7, 9*) so is not an adjustable parameter. Its temperature coefficient, $(d \ln a/dT)_p$, was treated as an adjustable parameter. The values obtained for the temperature coefficient

Table I. Debye-Hückel and Curve-Fitting Parameters

	$Ca(ClO_4)_2$	$Mn(ClO_4)_2$
$\phi°$, cal mol^{-1}	−6.7	−1.6
a, Å	5.7	5.8
$(d \ln a/dt)_p$, K^{-1}	0.000035	0.00013
K_H, cal l. mol^{-2}	−913	−377
J_H, cal l.^{2} mol^{-3}	198.6	261.5
Range of fit	0–2*M*	0–2*M*
σ, cal mol^{-1}	3.2	5.2

Table II. Relative Apparent Molar Enthalpies for $Ca(ClO_4)_2$

m, mol kg^{-1}	ϕ_L, cal mol^{-1} Obsd	ϕ_L, cal mol^{-1} Calcd	*m*, mol kg^{-1}	ϕ_L, cal mol^{-1} Obsd	ϕ_L, cal mol^{-1} Calcd
Titration run 1			Titration run 2		
0.003432	129	121	0.007725	167	167
0.01084	191	189	0.01529	217	214
0.01819	223	226	0.02653	256	255
0.03270	267	271	0.04127	287	289
0.04698	296	299	0.05575	309	312
0.06788	323	327	0.07806	332	336
0.08824	341	344	0.09872	348	351
0.1153	358	360	0.1274	363	365
0.1408	363	365	0.1531	372	374
0.1662	376	377	0.1913	381	382
0.2004	383	383	0.2278	386	386
0.2350	388	386	1.659	401	406
1.659	401	406			
Batch operation measurements					
0.007555	166	165	0.2350	390	386
0.01016	187	183	0.3091	394	388
0.01263	204	199	0.3813	392	385
0.01674	217	219	0.5245	377	376
0.02108	237	237	0.6653	373	366
0.02636	253	254	0.8383	360	358
0.03039	264	265	0.9687	356	355
0.008188	172	169	1.073	357	356
0.01084	191	189	1.389	365	373
0.01310	204	203	1.659	402	406
0.01590	217	216	2.015	481	475
0.01801	226	225	2.231	535	531
0.02050	235	235	2.734	718	720
0.02077	236	236	2.870	781	778
0.02215	241	241	3.037	852	855
0.02655	254	255	3.446	1058	1063
0.02654	255	255	3.879	1311	1309
0.02800	258	259	4.462	1669	1670
0.03399	272	274	5.254	2190	2194
0.03425	273	275	5.696	2508	2505
0.03921	283	285	6.607	3170	3168
0.03802	281	283	7.177	3607	3597
0.04292	290	292	7.686	3994	3997

Table III. Relative Apparent Molal Enthalpies for $Mn(ClO_4)_2$

m, mol kg^{-1}	ϕ_L, cal mol^{-1} Obsd	ϕ_L, cal mol^{-1} Calcd	*m*, mol kg^{-1}	ϕ_L, cal mol^{-1} Obsd	ϕ_L, cal mol^{-1} Calcd
Titration run 1			Titration run 2		
0.008728	193	177	0.01295	200	206
0.02610	266	264	0.03322	282	284
0.04323	307	308	0.06166	336	340
0.07594	357	360	0.08759	369	373
0.1082	389	393	0.1123	392	396
0.1549	422	425	0.1414	415	419
0.1956	444	445	0.1758	433	436
2.080	1182	1179	0.2054	447	450
			0.2418	462	464
			2.080	1182	1179
Batch operation measurements					
0.007983	168	171	0.2418	467	464
0.01239	203	202	0.3839	510	506
0.01722	229	228	0.5278	555	542
0.02043	240	242	0.6413	587	571
0.02778	274	269	0.8759	641	637
0.008849	179	178	1.060	691	698
0.009305	182	181	1.213	748	755
0.01378	210	210	1.606	918	927
0.01210	202	201	1.675	955	961
0.01396	212	212	1.827	1039	1040
0.01510	218	218	2.080	1185	1179
0.01576	221	222	2.389	1399	1398
0.01889	236	235	2.654	1609	1599
0.01981	241	240	3.321	2169	2169
0.02695	266	266	3.788	2620	2619
0.02741	268	268	4.206	3062	3062

Table IV. Selected Values of Relative Apparent Molal Enthalpies for $Ca(ClO_4)_2 \cdot nH_2O$ and $Mn(ClO_4)_2 \cdot nH_2O$ Solutions

n, mol H_2O	ϕ_L, cal mol^{-1} $Ca(ClO_4)_2$	ϕ_L, cal mol^{-1} $Mn(ClO_4)_2$	*n*, mol H_2O	ϕ_L, cal mol^{-1} $Ca(ClO_4)_2$	ϕ_L, cal mol^{-1} $Mn(ClO_4)_2$
∞	0	0	400	369	415
100000	54	54	300	381	441
50000	74	74	200	388	476
20000	110	111	150	386	503
10000	146	149	100	374	549
7000	168	171	75	362	598
5000	190	195	50	357	716
4000	206	211	40	373	828
3000	227	234	30	440	1053
2000	258	268	25	528	1263
1500	281	294	20	737	1697
1000	312	331	15	1208	2536
900	319	341	12	1777	...
800	328	352	10	2402	...
700	337	364	9	2842	...
600	347	378	8	3205	...
500	358	395			

are small, and it would be possible to obtain satisfactory fit with an assigned value of zero. The quantity ϕ° is a zero-point adjustment for the provisional values fitted, and K_H and J_H are coefficients of linear and squared terms in concentration. The equation was fitted in terms of concentrations rather than molalities. Fitting in terms of molality would be possible, with K_H and J_H absorbing most of the influence of the substitution.

Results and Discussion

Tables II and III give the observed and calculated values of ϕ_L at experimental molalities. The calculated values of ϕ_L are based on the Debye-Hückel function over its range of fit and on graphical or polynomial fit of the results at the higher molalities. Table IV gives values of ϕ_L at selected mole ratios. The uncertainty in ϕ_L is estimated at 2%, with an upper limit of ±30 cal mol^{-1} at the higher molalities.

Latysheva and Karavan (*2*) measured the enthalpies of dilution of a concentrated (saturated) solution of $Mn(ClO_4)_2$ and refer their enthalpies of solution for $Mn(ClO_4)_2 \cdot 6H_2O(s)$ to those measurements. Combination of their tabulated enthalpies of solution with values of ϕ_L from Tables III or IV leads to $\Delta H_{\mathrm{soln}}^\circ = (1.26 \pm 0.045)$ kcal mol^{-1} at 25°C. Values of ϕ_L obtainable from their results and scaled to the same reference point as ours run 60–90 cal mol^{-1} higher above 4*m*, as much as 70 cal mol^{-1} lower at 3*m*, about 50–70 cal mol^{-1} higher at 1*m*, and 45–55 cal mol^{-1} lower from 0.17 to 0.07*m*. The deviations are larger than those observed for their measurements on $Ni(ClO_4)_2$ compared to ours. The general shape of their ϕ_L curve for $Mn(ClO_4)_2$ conforms to ours, with the deviations occurring in "runs" or sequences of points, rather than being systematic. The pattern of deviations does not correspond to that which would arise from traces of $HClO_4$ in the solutions, and the preparative procedures and tests on our solution of $Mn(ClO_4)_2$ indicate that its level of acidity would be too low to produce thermal perturbations of such magnitude.

The ϕ_L curve for $Mn(ClO_4)_2$ lies close to that for $Mg(ClO_4)_2$, actually slightly above, and suggests that Mn^{2+} is possibly more strongly hydrated, and a better "structure maker" than Mg^{2-}. The curve for $Ca(ClO_4)_2$ lies about where expected in relation to $Mg(ClO_4)_2$ and $Sr(ClO_4)_2$, corresponding to a degree of hydration intermediate between those cations, with corresponding difference in its influence on water structure. Considering this behavior, the ion-size parameter for $Ca(ClO_4)_2$, 5.7 Å, would be expected to be slightly less than that, 5.6 Å, for $Mg(ClO_4)_2$ (*7, 9*). However, values of *a* from activity coefficient data may easily be uncertain by ±0.2 Å.

Our values of ϕ_L for $Ca(ClO_4)_2$ tend to run lower than those tabulated in NBS Technical Note 270-6 (*6*), with differences of over 100 cal mol^{-1} at some molalities. The tabulated values are given to ±10 cal mol^{-1}, and the uncertainty in the original data may have been substantially greater.

The primary experimental data for this paper are given in Tables V and VI (deposited with the ACS Microfilm Depository Service).

Acknowledgment

The equipment from the University of Nebraska Research Council is gratefully acknowledged.

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Received for review May 20, 1974. Accepted July 19, 1974. The junior author (L. J. G.) received a NDEA Title IV Fellowship from the U.S. Government. This paper presents part of the work presented in the PhD thesis of L. J. G. in 1974.

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