

Enthalpies of Dilution and Relative Apparent Molar Enthalpies of Aqueous Copper Perchlorate

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Enthalpies of dilution for $\text{Cu}(\text{ClO}_4)_2$ solutions were measured by solution calorimetry at 298.15K. Values of ϕ_L , the relative apparent molar enthalpy, were obtained over the range 0–4.65*m*. A form of the Debye-Hückel equation guided extrapolation to $m = 0$. The ϕ_L curve for $\text{Cu}(\text{ClO}_4)_2$ indicated a looser hydration shell for Cu^{2+} than for Ni^{2+} or Zn^{2+} , probably owing to distortion of the coordination sphere for Cu^{2+} by the Jahn-Teller effect. The ϕ_L values were combined with literature data to calculate $\Delta H_{\text{soln}}^\circ = (4550 \pm 90) \text{ cal mol}^{-1}$ for $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}(\text{s})$.

This paper is part of a series of studies on the relative apparent molar enthalpies, ϕ_L , of the 2–1 perchlorates (1, 11). These salts, highly soluble and free from complex ion formation, provide an extensive series for comparison of ion size, ion hydration, and other factors influencing the values of ϕ_L . The only existing data for $\text{Cu}(\text{ClO}_4)_2$ are those obtainable indirectly from measurements of the enthalpy of solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ at various molalities by Shchukarev et al. (7), over the range of 0.1*m* to near saturation. Their results were obtained with a microcalorimeter, and the listed uncertainty is $\pm 50 \text{ cal mol}^{-1}$. In this mode of measurement, errors from variation in stoichiometry of the hydrate are difficult to control.

In their studies on the activity coefficient of $\text{Cu}(\text{ClO}_4)_2$ solutions, Libus and Sadowska (5) compared the activity coefficients with those for $\text{Ni}(\text{ClO}_4)_2$, $\text{Co}(\text{ClO}_4)_2$, and $\text{Mg}(\text{ClO}_4)_2$ and suggested that part of the small difference observed might be due to the Jahn-Teller effect on the energy states of Cu^{2+} , leading to a distorted and slightly unsymmetrical coordination sphere, wherein some of the water molecules might be less firmly bound (2, 7). The relative apparent molar enthalpy, ϕ_L , should be much more sensitive to such effects. The results obtained in this paper show pronounced differences in ϕ_L behavior for $\text{Cu}(\text{ClO}_4)_2$ solutions as compared to $\text{Mg}(\text{ClO}_4)_2$ and several of the perchlorates of the first row transition elements, corresponding to less firmly bound water in the hydration sphere.

Experimental

Materials and analyses. Basic copper carbonate was dissolved in 30% perchloric acid solution. The solution was warmed on a steam bath for several hours, then filtered to remove excess copper carbonate, and was heated to 100–120°C to remove CO_2 and solvent. Upon cooling, a large crop of crystals was obtained. These were separated by filtration, rinsed with a fine spray of ice-cold water, and then dissolved in twice distilled water to form a nearly saturated solution at laboratory temperatures. The acidity of the stock solution was adjusted so that a portion diluted 1 to 100 with twice distilled water had a pH of 4.7. This level of acidity was considered prudent to suppress hydrolysis (8) and should be low enough to produce no significant error in the dilution measurements.

The distilled water used as diluent was made to $10^{-4}m$ with HClO_4 to suppress possible hydrolysis effects in dilute

solutions. This amount of HClO_4 should have negligible effects on the enthalpies of dilution.

The stock solution of $\text{Cu}(\text{ClO}_4)_2$ was analyzed by weight buret techniques with standard EDTA, following procedures described by Welcher (13). The EDTA was standardized as recommended against metallic zinc and primary standard CaCO_3 . Precision of standardizations was 0.01–0.02%. Analyses of some calorimetric solutions after dilution were made by iodometric procedures according to Kolthoff and Belcher (3). The results of different analyses agreed to 0.02%. Working solutions were prepared from the stock solution by mass dilutions. Densities of the $\text{Cu}(\text{ClO}_4)_2$ solutions, for buoyancy corrections, were taken from data of Latysheva et al. (4). Concentrations M were computed from the molalities m as needed, based on these densities.

Calorimetric apparatus and procedures. The calorimeter and components have been described (1, 9–11). As for other

Table I. Relative Apparent Molar Enthalpies for $\text{Cu}(\text{ClO}_4)_2$

<i>m</i> , mol kg ⁻¹	ϕ_L , cal mol ⁻¹		<i>m</i> , mol kg ⁻¹	ϕ_L , cal mol ⁻¹	
	Obsd	Calcd		Obsd	Calcd
Titration run 1					
0.001856	97	92	0.002764	112	111
0.006475	156	155	0.009596	193	181
0.01557	214	215	0.02307	246	244
0.02452	245	249	0.03629	279	279
0.03759	277	283	0.05567	310	313
0.05447	306	311	0.08069	336	340
0.07471	331	334	0.1049	353	357
0.09408	347	350	0.1282	365	368
0.1162	361	363	0.1617	377	380
0.9655	397	406	0.1936	385	387
			1.451	458	472
Batch operation measurements ^a					
0.006506	155	156	0.1936	386	387
0.006605	158	156	0.1936	387	387
0.006607	158	156	0.1936	389	387
0.009204	183	178	0.2791	399	396
0.003847	121	126	0.4683	410	397
0.004531	135	134	0.5367	406	396
0.01809	227	225	0.5628	403	395
0.007479	165	164	0.9173	403	403
0.008741	175	174	1.090	417	417
0.009928	184	184	1.338	452	451
0.01269	201	200	1.448	468	471
0.01719	221	222	2.079	651	643
0.01982	232	233	2.365	787	790
0.02232	241	241	2.798	1030	1028
0.02409	246	247	3.149	1248	1253
0.02951	262	264	3.817	1751	1745
0.03170	268	269	4.172	2037	2041
0.03353	272	273	4.653	2482	2483

^a For each line, the entries in columns 1 and 4 represent related final and initial molalities, respectively, for that run. The corresponding entries in columns 2 and 5 permit recovery of the experimental quantity $\Delta\phi_L = \phi_5 - \phi_2$, where the subscripts refer to the column numbers.

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Table II. Selected Values of ϕ_L for $\text{Cu}(\text{ClO}_4)_2 \cdot n\text{-H}_2\text{O}$

n of H_2O	Molality	ϕ_L , cal mol ⁻¹
∞	0.000000	0
100,000	0.0005556	54
50,000	0.001111	74
20,000	0.002778	110
10,000	0.005556	146
7,000	0.007937	168
5,000	0.01111	191
4,000	0.01389	206
3,000	0.01852	228
2,000	0.02778	259
1,500	0.03704	281
1,000	0.05556	313
900	0.06173	321
800	0.06944	329
700	0.07937	339
600	0.09259	349
500	0.1111	360
400	0.1389	373
300	0.1851	385
200	0.2778	396
150	0.3704	398
100	0.5556	395
75	0.7407	396
50	1.111	419
40	1.389	460
30	1.852	571
25	2.222	694
20	2.778	1013
15	3.704	1654

dilution studies in this laboratory, temperatures were measured to 10^{-5} K with a Hewlett-Packard quartz thermometer (HP-M40-2801A), and the thermostat was controlled to ± 0.0005 K or better.

The pulse titration procedure (1, 9) was used to obtain ϕ_L data at low molalities, up to 0.25 m , and batch-type operations were used to delineate the remainder of the ϕ_L curve.

Treatment of experimental data. All calculations were performed by digital computer. The procedures for reduction of the original calorimetric data and for assembly of provisional values for the apparent molar enthalpy, ϕ_L' , vs. $m^{1/2}$ curves have been described elsewhere (1, 9).

The provisional values, ϕ_L' , were fitted to the Debye-Hückel function as for other investigations (9, 11) by a least-squares procedure. The ion-size parameter, $a = 5.7$ Å, for $\text{Cu}(\text{ClO}_4)_2$ was based on reported activity coefficients (5) and is not an adjustable parameter. The parameters for best fit were: $\phi^\circ = -1.75$ cal mol⁻¹, where ϕ° is a zero-point adjustment needed to obtain ϕ_L from the provisional set of ϕ_L' values ($\phi_L = \phi_L' - \phi^\circ$); $(d \ln a/dT)_p = 3 \times 10^{-5}$ K⁻¹, the temperature coefficient of a ; $K_H = -863$ cal mol⁻² dm³, and $J_H = 235.5$ cal mol⁻³ dm⁶, where K_H and J_H are coefficients of linear and squared terms in concentration. The standard deviation, σ , was 4.65 cal mol⁻¹ for the range 0–2.0 mol dm⁻³. The Debye-Hückel equation was fitted in terms of concentrations, rather than molalities, primarily to secure a less ambiguous value for $(d \ln a/dT)_p$. The value for the temperature coefficient in this case is so nearly zero that it could have

been omitted, in which case an equally good fit could have been obtained with slightly different values for K_H and J_H .

Results and Discussion

Table I gives experimental and calculated values of ϕ_L referred to a common reference point at $m = 0$. The experimental values are based on interlocking groups of values which were fitted to the Debye-Hückel function (9, 11). The calculated values are based on the Debye-Hückel function up to 2 m and on graphical smoothing above that molality. Table II gives smoothed values of ϕ_L at selected molalities and mole ratios. The uncertainties in ϕ_L are estimated at 2%, up to a maximum of ± 30 cal mol⁻¹, based on calorimetric performance and analytical contributions. Table III (deposited with the ACS Microfilm Depository Service) contains the primary experimental data for this paper.

The curve of ϕ_L vs. $m^{1/2}$ is characterized by a long region of small slope and small curvature from 0.2 to 1.2 m , and the main part of the curve lies well below those for the perchlorates of other first row transition elements (Mn, Ni, Co, Zn) (1, 12). Indeed, the curve for $\text{Cu}(\text{ClO}_4)_2$ lies only slightly above that for $\text{Ca}(\text{ClO}_4)_2$ over its whole range. From this behavior we infer that the intensity of hydration for Cu^{2+} resembles closely that for Ca^{2+} , and that in the region 0.2–1.2 m , the ions are about equivalent in their "structure-breaking" effect on the solvent water. The marked difference between Cu^{2+} and the other first row transition elements seems clearly to be due to the loosened and distorted first shell hydration layer as a result of the Jahn-Teller effect on Cu^{2+} , with the disruption affecting second-layer hydration as well.

From the measurements by Shchukarev et al. (7) and values of ϕ_L from Table I or II, we obtain for the standard enthalpy of solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}(\text{s})$, $\Delta H_{\text{soln}}^\circ = (4550 \pm 90)$ cal mol⁻¹. The ϕ_L curve obtainable from their data does not conform to ours within their stated uncertainties, and there are systematic trends in the differences.

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Supplementary Material Available. Table III 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, 24X 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 \$4.00 for photocopy or \$2.50 for microfiche, referring to code number JCED-75-259.