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Apparent molar heat capacities and volumes for $HClO_4$(aq) to 373 K

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Abstract

Heat capacities of aqueous $HClO_4$ solutions from 298.15 to 373.15 K, and densities from 296.02 to 371.82 K, have been measured at 0.5 MPa using a flow, differential heat capacity calorimeter and, in series, a vibrating-tube densimeter. Equations for the apparent molar heat capacities and volumes are reported as a function of temperature, and values for the ionic partial molar heat capacities and volumes of $HClO_4$(aq) are estimated. The experimental apparent molar heat capacities are compared with disparate values reported in the literature.

Keywords: Apparent molar heat capacities; Apparent molar volumes; Aqueous perchloric acid; Temperature dependence

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1. Introduction

Chemical thermodynamic data for aqueous solution species are required for modelling the behaviour of radionuclides for nuclear waste disposal. Most of the available literature values for equilibrium constants, solubilities, and enthalpies of solution are of temperatures near 300 K. However, values for higher temperatures (to 400 K for nuclear fuel waste disposal calculations) are often required.

Recently we reported a series of flow microcalorimetry measurements and density measurements for [NpO_2ClO_4(aq) + $HClO_4$(aq)] solutions near 300 K [1], and have extended these measurements to temperatures from 290 to 370 K [2]. However, to obtain apparent molar heat capacities ($C_{p,2,\Phi}$) and volumes ($V_{2,\Phi}$) for NpO_2ClO_4(aq)

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from data for solutions also containing $HClO_4$(aq), values of $C_{p,2,\Phi}$ and $V_{2,\Phi}$ for $HClO_4$(aq) are required at the total ionic strengths of the solutions [1–3]. Temperature dependent values of $C_{p,2,\Phi}$ have been reported by Pogue and Atkinson [4] (288.15–328.15 K) and Hovey et al. [5, 6] (283.15–328.15 K), but the results from these studies differ markedly, especially at higher temperatures. Furthermore, neither study provides $C_{p,2,\Phi}$ values for temperatures above 328.15 K. Therefore, differential heat capacity measurements have been carried out for $HClO_4$(aq) solutions for temperatures from 298.15 to 373.15 K and differential densities have been measured from 296.02 to 371.82 K.

2. Experimental

The flow-heat-capacity microcalorimeter and the flow-vibrating-tube densimeter were the same as those used for our earlier measurements on $NaTcO_4$(aq) [7], and most of the procedures used for the measurements were the same as those described in detail elsewhere [7–9]. The electrical circuits for the calorimeter were calibrated using H_2O(l) before or just after each day's experiments, and measurements for solutions ofNaCl(aq) were also made, usually within a day of the measurements on each set of $HClO_4$(aq) solutions. These provided a chemical standard for the measurements. The densimeter was standardized using NaCl(aq) or N_2(g).

Stock perchloric acid solutions were prepared from several different lots of concentrated acid (BDH and Fisher Scientific). The stocks were diluted by weight and analysed using solutions of NaOH(aq) that had been standardized against primary standard grade potassium hydrogen phthalate. For the flow calorimetry measurements for $HClO_4$(aq), five different lots of acid were used to prepare seven stocks (designated A–G in Table 1), and other solutions were prepared by weight from these stock solutions. Heat capacity measurements were carried out at temperatures from 298.15 to 373.15 K. Solution molalities of $HClO_4$(aq) ranged from 0.1 to 1.6 mol kg^{-1} at 298.15 K, but to limit possible corrosion problems, the acid molalities were restricted to $\leq$0.62 mol kg^{-1} at the higher temperatures. The calorimeter was calibrated, usually within a day of each experiment, using 1 molal solutions of NaCl(aq). Comparison values for NaCl(aq) were calculated using a program originally supplied by D.G.

Table 1
Apparent molar heat capacities and apparent molar volumes of $HClO_4$(aq) as a function of temperature at 0.5 MPa

Stock	$m(HClO_4(aq))^a$	$10^2(c_p\rho/c^*_{p,1}\rho^*_1-1)$	$C_{p,2,\Phi}{}^a$	$(\rho-\rho^*_1)^a$	$V_{2,\Phi}{}^a$
		298.15 K		296.02 K	
Fd	0.1026	−0.4818	−14.1	5.768	43.9^b
Gd	0.1035	−0.4838	−13.1	5.821	43.9^b
Aa	0.2050	−0.9657	−17.4	11.568	43.5
Ca	0.2057	−0.9658	−15.0	11.522	43.9
Ec	0.2816	−1.2982	−13.2	15.796	43.6
Aa	0.4103	−1.8590	−10.7	22.868	43.7

Table 1 (*Continued*)

Stock	$m(\mathrm{HClO_4(aq)})^a$	$10^2(c_p\rho/c^*_{p,1}\rho^*_1-1)$	$C_{p,2,\Phi}$ [a]	$(\rho-\rho^*_1)^a$	$V_{2,\Phi}$ [a]
Aa	0.4116	−1.8648	−10.4	22.915	43.8
Ac	0.5710	−2.5068	−4.9	31.455	44.0
Bb	0.6138	−2.6869	−5.0	33.806	43.9
Db	0.6158	−2.6811	−2.9	33.739	44.2
Ec	0.7791	−3.3155	−0.9	42.580	43.9
Ab	0.8355	−3.5266	−0.5	45.678	43.8
Cb	0.8391	−3.5391	0.1	45.763	43.9
Ab	0.9804	−4.0647	1.0	53.431	43.6
Cb	0.9853	−4.0892	1.5	53.524	43.8
Bc	1.1626	−4.7212	3.4	62.888	43.6
Dc	1.1665	−4.7211	4.7	62.880	43.8
Ba	1.4694	−5.7762	6.4	78.676	43.5
Da	1.4771	−5.7455	10.1	78.344	44.0
Ec	1.6106	−6.1547	11.5	85.231	43.8
			313.15 K	311.06 K	
Ca	0.2057	−0.9294	0.2	11.083	46.0
Ea	0.2816	−1.2561	−0.1	15.262	45.5
Ca	0.4116	−1.8133	2.3	22.062	45.8
Ea	0.5710	−2.4520	4.8	30.530	45.5
Eb	0.7791	−3.2491	8.7	41.228	45.6
Ab	0.8335	−3.4700	8.5	44.199	45.5
Ab	0.9804	−4.0078	9.8	51.649	45.4
			328.15 K	326.10 K	
Ca	0.2057	−0.9294	4.4	10.804	47.3
Cb	0.2057	−0.9294	4.7	10.788	47.4
Ea	0.2816	−1.2574	5.1	14.796	47.1
Eb	0.2816	−1.2600	4.9	14.785	47.2
Ca	0.4116	−1.8048	8.5	21.388	47.4
Ea	0.5710	−2.4554	9.9	29.582	47.2
Aa	0.8355	−3.4894	12.1	42.977	46.9
			348.15 K	346.10 K	
A	0.2050	−0.9344	5.4	10.521	48.5
C	0.2057	−0.9422	5.9	10.487	48.9
E	0.2816	−1.2666	7.8	14.362	48.7
A	0.4103	−1.8137	9.7	20.832	48.6
C	0.4116	−1.8196	11.0	20.762	48.9
E	0.5710	−2.4679	13.1	28.701	48.7
B	0.6138	−2.6675	10.5	30.956	48.4
			373.15 K	371.82 K	
Aa	0.2050	−0.9671	0.3	10.267	49.8
Cb	0.2057	−0.9812	−2.0	10.302	49.8
Eb	0.2816	−1.3139	1.7	14.052	49.8
Aa	0.4103	−1.9037	1.7	20.349	49.8
Ca	0.4116	−1.9188	2.1	20.279	50.1
Ea	0.5710	−2.5923	4.9	28.056	49.9
Ba	0.6138	−2.7807	4.2	30.206	49.7

[a] Units: m/mol kg^{-1}; $C_{p,2,\Phi}$/J K^{-1} mol^{-1}; ρ/kg m^{-3}; $V_{2,\Phi}$/cm^3 mol^{-1}.

[b] 0.57 MPa, all other measurements at 0.50 MPa.

Archer, and modified by the present authors for use on a VAX computer system. The calculated values are those of Archer [10]. From the values for NaCl(aq), calibration values "f" were calculated [11]. The "f" factors were generally 1.00 ± 0.02, but varied with temperature and from day-to-day. As applied here, they undoubtedly assimilated a number of random and systematic errors.

3. Results and discussion

The experimentally determined values of the quantities $(c_p\rho/c^*_{p,1}\rho^*_1 - 1)$ and $(\rho - \rho^*_1)$ for $HClO_4$(aq) are provided in Table 1. The values of $(c_p\rho/c^*_{p,1}\rho^*_1 - 1)$ and $(\rho - \rho^*_1)$ in Table 1 represent the average of at least two experimental runs, and the values of $(c_p\rho/c^*_{p,1}\rho^*_1 - 1)$ in Table 1 have been adjusted using the chemical calibration factor "f" as described above. In these expressions, $\rho/\mathrm{kg\,m^{-3}}$ is the solution density, ρ^*_1 is the density of the pure solvent (water) at the temperature and pressure of the experiment, $c_p/\mathrm{J\,K^{-1}\,g^{-1}}$ is the specific heat capacity of the solution and $c^*_{p,1}$ is the specific heat capacity of the pure solvent at the temperature and pressure of the experiment. Values of $C_{p,2,\Phi}$ are calculated from the experimental specific heat capacity measurements according to

$$C_{p,2,\Phi}(T, m) = M_2 c_p(T, m) + [c_p(T, m) - c^*_{p,1}(T)]/m \tag{1}$$

where M_2 is the molar mass of the solute and m is the molality of the solute. The apparent molar volumes $(V_{2,\Phi}/\mathrm{m^3\,mol^{-1}})$ are calculated from the density data using the equation

$$V_{2,\Phi}(T, m) = M_2/\rho(T, m) - [\rho(T, m) - \rho^*_1(T)]/[m\rho^*_1(T)\rho(T, m)] \tag{2}$$

The reference values for pure water are those of Hill [12] and Archer and Wang [13] as used by Archer [10] in his recent assessment of values for NaCl(aq).

In Table 1, solutions prepared from the different stocks of acid are identified by upper case letters (A–G). Calorimetric results obtained on the same day at the same temperature are denoted by a lower case letter as part of the stock identification. There do not seem to be any systematic differences attributable to the different stocks or to different behaviour of the calorimeter on different days. As noted above, the results for $HClO_4$(aq) reported by Pogue and Atkinson [4] (288.15–328.15 K) and Hovey et al. [5,6] (283.15–328.15 K), differ markedly. Also, values of $C_{p,2,\Phi}(HClO_4(aq))$ can be calculated from the approximate relationship

$$C_{p,2,\Phi}(HClO_4(aq)) = C_{p,2,\Phi}(HCl(aq)) + C_{p,2,\Phi}(KClO_4(aq)) - C_{p,2,\Phi}(KCl(aq)) \tag{3}$$

making use of experimental results for KCl(aq), $KClO_4$(aq) and HCl(aq) [8,9,14]. These yield values for $C_{p,2,\Phi}(HClO_4(aq))$ similar to those of Pogue and Anderson at 298.15 K, but intermediate between the two sets of directly determined values (Fig. 1) for 328.15 K. The results from this calculation are limited, as the low solubility of $KClO_4$(cr) in water precluded measurements of $C_{p,2,\Phi}(KClO_4(aq))$ for $KClO_4$(aq) molalities greater than 0.12 mol kg^{-1} [8].

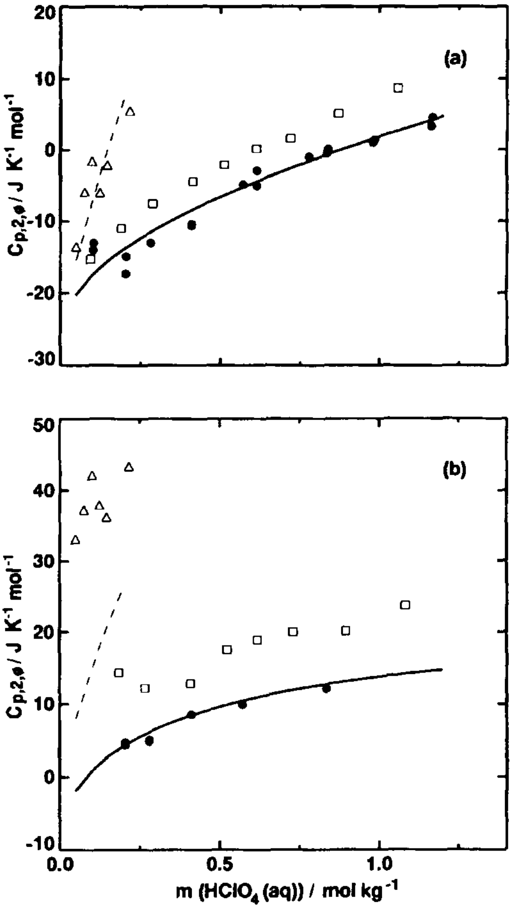

Fig. 1. Apparent molar heat capacities for $HClO_4$(aq) at 298.15 K (a) and 328.15 K (b) as determined by Hovey et al. [5, 6] (□); Pogue and Atkinson [4] (△); and the present work (●). The solid line represents the best fit line of Eq. (4), at the specified temperature, to the values determined in the present work for all temperatures. The dashed line represents the values calculated from the temperature-dependent apparent molar heat capacities [8, 9, 14] of HCl(aq), $KClO_4$(aq) and KCl(aq) (Eq. (3)).

As shown in Fig. 1, our apparent molar heat capacity results for $HClO_4$(aq) are parallel to, but systematically more negative by 5–8 J K^{-1} mol^{-1} than, those of Hovey et al. [5, 6] (the values for solutions F and G in Table 1 are those referred to briefly in our earlier paper [1]). The results of Pogue and Atkinson [4] are much more positive than either of the other sets of direct experimental values, and increase more sharply with increasing concentration. The differences are greater at 328.15 K than at 298.15 K, increasing to almost 40 J K^{-1} mol^{-1}.

The apparent molar heat capacities of Pogue and Atkinson [4] for HCl(aq) similarly differ from those Allred and Woolley [14], and also appear to be more positive than those of Saluja et al. [8]. This suggests some systematic problem in the experimental heat capacity experiments of Pogue and Atkinson [4]. If this is true, it indicates a problem also exists with the literature $C_{p,2,\Phi}$ values for at least one of $KClO_4$(aq) [8], KCl(aq) [9] or HCl(aq) [8, 14], with the values for $KClO_4$(aq) most likely to be suspect because $KClO_4$ (cr) is only sparingly soluble in water near room temperature.

Pitzer-type equations [15, 16] of the form

$$C_{p,2,\Phi} = C^0_{p,2} + (A_J/b)\ln(1 + bI^{0.5}) - 2RT^2 m\,\beta^{(0)J} \tag{4}$$

where
$$C^0_{p,2} = p_{c1}/T + p_{c2} + p_{c3}T$$
$$\beta^{(0)J} = p_{c4}/T + p_{c5} + p_{c6}T$$
$$A_J = (\partial A_H/\partial T)_p$$

were fitted to the apparent molar heat capacities from our work and that of Hovey et al. [5, 6], as described previously [7, 9]. The parameter b is an arbitrary constant in the Pitzer equations and is assigned the value 1.2 $kg^{1/2}$ $mol^{1/2}$, I is the molal ionic strength, T is the Kelvin temperature, and A_J and A_H are the theoretical limiting Debye–Hückel slopes for enthalpies and partial molar heat capacities [17], respectively. The fitting parameters (0.6 MPa) are reported in Table 2, and calculated values of the partial molar heat capacities at several temperatures are reported in Table 3.

Table 2
Fitted parameters (0.6 MPa) for the temperature and molality dependence of the apparent molar heat capacities of $HClO_4$(aq) (Eq. (4))

Parameter	Value
$10^{-5}p_{c1}$	−5.45295
$10^{-3}p_{c2}$	3.25118
p_{c3}	−4.86333
$10^{2}p_{c4}$	−9.44688
$10^{4}p_{c5}$	5.22218
$10^{7}p_{c6}$	−7.09945

Table 3
Partial molar heat capacities for $HClO_4$(aq) at selected temperatures

T/K	$C^{o}_{p,2}$/J K^{-1} mol^{-1}
283.15	−51.7
298.15	−27.8
313.15	−13.1
323.15	−7.8
328.15	−6.4
348.15	−8.3
373.15	−24.9

Our apparent molar volumes are systematically less positive than those reported by Hovey et al. [5, 6], Pogue and Atkinson [4] and Herrington et al. [18]. The differences (of the order of 1 $cm^3 mol^{-1}$) may be related in part to small errors in the concentrations of $HClO_4$ (aq), as an uncertainty of 0.5% in the molalities would be propagated into an uncertainty of 0.3 $cm^3 mol^{-1}$ in the value of an apparent molar volume. Our apparent molar volume values and those of Hovey et al. [5,6], equally weighted, were used only to make the minor adjustment of the apparent molar heat capacity values to a common pressure (0.6 MPa). As our primary interest in this work was to determine the apparent molar heat capacities, the apparent inconsistency in the density results (as reflected in the calculated apparent molar volumes) was not investigated further.

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