

APPARENT MOLAR HEAT CAPACITIES AND VOLUMES OF AQUEOUS HClO_4 , HNO_3 , $(\text{CH}_3)_4\text{NOH}$ AND K_2SO_4 AT 298.15 K

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ABSTRACT

Apparent molar heat capacities and volumes of $\text{HClO}_4(\text{aq})$, $\text{HNO}_3(\text{aq})$, $(\text{CH}_3)_4\text{NOH}(\text{aq})$ and $\text{K}_2\text{SO}_4(\text{aq})$ have been determined at 298.15 K. Infinite dilution standard state partial molar heat capacities and volumes have been calculated from these data. We recommend revised values for the conventional ionic partial molar heat capacities and volumes of $\text{ClO}_4^- (\text{aq})$, $\text{NO}_3^- (\text{aq})$ and $\text{SO}_4^{2-} (\text{aq})$.

INTRODUCTION

As part of our continuing research on the thermodynamic properties of aqueous solutions, we have made calorimetric and densimetric measurements on aqueous solutions of HClO_4 , HNO_3 , $(\text{CH}_3)_4\text{NOH}$ and K_2SO_4 at 298.15 K. Our new results permit evaluation of standard state (infinite dilution) partial molar properties of these aqueous electrolytes, from which we have deduced improved values for the corresponding properties of some of the constituent ions of these electrolytes.

Our specific reasons for making measurements on solutions of these electrolytes arose from our need for these results in connection with some other investigations. For example, we needed knowledge of apparent molar heat capacities and volumes of aqueous HClO_4 and HNO_3 over wide ranges of concentration in order to calculate desired apparent molar heat capacities and volumes of $\text{Fe}(\text{ClO}_4)_3$ [1], $\text{UO}_2(\text{ClO}_4)_2$ [2], $\text{Hg}(\text{ClO}_4)_2$ and $\text{Pb}(\text{ClO}_4)_2$ [3] and $\text{UO}_2(\text{NO}_3)_2$ [4] from the measured properties of acidic solutions containing these salts. We had a similar need for knowledge of properties of solutions of $(\text{CH}_3)_4\text{NOH}$ in connection with our measurements on alkaline solutions of EDTA [5].

EXPERIMENTAL

Water to be used for all experiments was passed through an activated charcoal filter and then through a Milli-RO4/Milli-Q reagent grade mixed bed ion exchange column and activated carbon system to yield purified water with a resistivity of 18 M Ω cm or greater. Concentrated perchloric and nitric acids were obtained from Fisher (certified, ACS) and were used without further purification. A 25% aqueous solution of tetramethylammonium hydroxide was obtained from Alfa (certified, ACS) and was used without further purification. Certified K₂SO₄ was obtained from Fisher.

Stock solutions of HClO₄, HNO₃ and (CH₃)₄NOH were prepared from the concentrated aqueous solutions by dilution with water. The acids were standardized by titration against tris(hydroxymethyl)-aminomethane (THAM). The stock solution of (CH₃)₄NOH was standardized by titration against potassium hydrogen phthalate (KHP). The stock solution of K₂SO₄ was prepared by mass after drying the salt at 110 °C.

Densities and heat capacities of our solutions were measured with a Sodev model 03D Picker flow densimeter [6] and a Sodev model CP-C Picker flow microcalorimeter [7]. Both the densimeter and calorimeter were controlled to (298.15 ± 0.01) K and held at constant (± 0.001 K) temperature with separate Sodev model CT-L circulating baths. The operating temperatures for both instruments were monitored with thermistors that had been calibrated against a Hewlett-Packard 2804A quartz thermometer and placed in the circulating fluid lines immediately before the measurement cells.

The densimeter was calibrated with water and concentrated (0.95–1.00 molal) solutions of NaCl [6]. Measured heat capacities were corrected for small heat leaks as suggested by Desnoyers et al. [8]; the correction factor was evaluated daily and was found to be 1.006 ± 0.002.

RESULTS AND CALCULATIONS

Results of measurements with the Picker flow calorimeter are volumetric heat capacities (J K⁻¹ cm⁻³). Combination of these with the densities that we have also measured permits calculation of specific heat capacities (J K⁻¹ g⁻¹) and thence the desired apparent molar heat capacities ϕC_p of the solutes. Similarly, densities of the solutions lead to apparent molar volumes ϕV of the solutes. These apparent molar heat capacities and volumes are defined by equations of the type

$$\phi Y = [Y(\text{sln}) - n_1 Y_1^*] / n_2 \quad (1)$$

in which $Y(\text{sln})$ is the extensive property (heat capacity or volume) of a specified quantity of solution, n_1 is the amount (moles) of solvent in this specified quantity of solution, Y_1^* is the molar property (heat capacity or

TABLE 1

Results of calorimetric and densimetric measurements at 298.15 K

m (mol kg ⁻¹)	ϕV (cm ³ mol ⁻¹)	ϕC_p (J K ⁻¹ mol ⁻¹)
HClO₄		
1.0588	44.65	8.79
0.87073	44.71	5.22
0.71850	44.71	1.63
0.61269	44.72	0.21
0.51356	44.72	-2.08
0.41412	44.71	-4.44
0.28819	44.72	-7.56
0.19110	44.54	-11.01
0.09494	44.45	-15.39
HNO₃		
1.1115	30.23	-
1.1115	30.26	-31.84
0.85809	30.22	-37.07
0.81123	30.22	-38.62
0.61416	30.18	-43.11
0.47135	30.15	-46.75
0.34271	30.08	-50.90
0.22793	30.02	-54.43
0.11160	29.91 ^a	-58.32 ^a
(CH₃)₄NOH		
0.88135	85.93	122.7
0.88135	85.84	-
0.68384	85.97	117.9
0.60701	86.04	116.4
0.49297	86.04	115.3
0.35938	86.07	110.9
0.29242	86.07	108.9
0.20339	86.08	106.9
0.10948	86.12 ^a	103.4
K₂SO₄		
0.49662	40.58	-121.8
0.40229	39.80	-136.7
0.32377	39.04	-148.7
0.32377	39.04	-
0.25841	38.25	-161.4
0.17242	37.15	-179.3
0.11097	36.18	-195.8
0.07858	35.50	-205.8
0.03623	34.20 ^a	-223.7 ^a

^a These values were not used in our least-squares analyses, but are shown in the figures.

volume) of pure solvent (water) and n_2 is the amount (moles) of solute in the specified quantity of solution. Directly useful equations for these calculations, which also permit recovery of our experimental specific heat capacities and densities, are the following

$$\phi V = \left\{ \left[(1 + mM_2) / \rho \right] - (1 / \rho_1^*) \right\} / m \quad (2)$$

$$\phi C_p = \left[c_p (1 + mM_2) - c_{p,1}^* \right] / m \quad (3)$$

In these equations m is the molality of the solution, M_2 is the molar mass of the solute, ρ and ρ_1^* are the densities of solution and of pure water, respectively, and c_p and $c_{p,1}^*$ are the specific heat capacities of solution and of pure water, respectively. We have used $c_{p,1}^* = 4.1793 \text{ J K}^{-1} \text{ g}^{-1}$ and $\rho_1^* = 0.997047 \text{ g cm}^{-3}$ from Kell [9,10].

Results of all of our measurements are summarized in Table 1.

Apparent molar properties of solutions of aqueous electrolytes are represented satisfactorily to moderate ionic strengths by Debye-Hückel equations of the form

$$\phi Y = \phi Y^\ominus + A_Y \omega I^{1/2} + B_Y I + C_Y I^{3/2} \quad (4)$$

in which ϕY^\ominus is the desired standard state (infinite dilution) partial molar property, A_Y is the Debye-Hückel limiting slope, ω is the "valence factor", I is the ionic strength, and B_Y and C_Y are adjustable parameters. The ionic strength, valence factor and molality are related by

$$I = \omega m = 0.5 \sum m_i z_i^2 \quad (5)$$

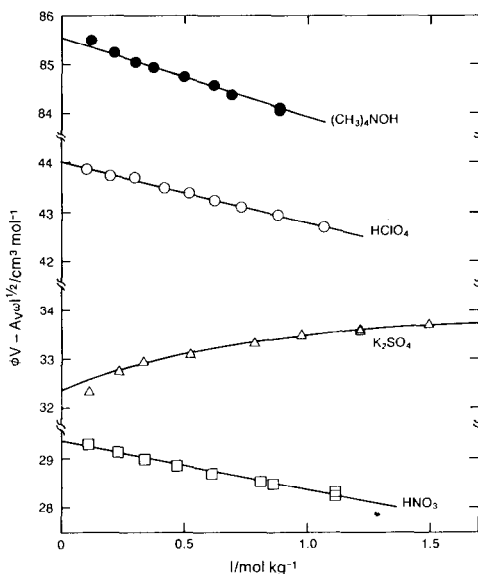


Fig. 1. ϕV minus the Debye-Hückel limiting slope ($A_Y \omega I^{1/2}$) for aqueous HClO_4 , HNO_3 , $(\text{CH}_3)_4\text{NOH}$ and K_2SO_4 against I . Lines are least-squares fits of eqn. (4).

TABLE 2

Standard state (infinite dilution) partial molar heat capacities, volumes, B_V and C_V parameters at 298.15 K^a

Solute	${}^\phi V_i^\ominus$ ($\text{cm}^3 \text{ mol}^{-1}$)	B_V ($\text{cm}^3 \text{ kg mol}^{-2}$)	C_V ($\text{cm}^3 \text{ kg}^{5/2} \text{ mol}^{-3/2}$)	${}^\phi C_p^\ominus$ ($\text{J K}^{-1} \text{ mol}^{-1}$)	B_C ($\text{J K}^{-1} \text{ kg mol}^{-2}$)	C_C ($\text{J kg}^{3/2} \text{ K}^{-1} \text{ mol}^{-5/2}$)
HClO ₄	43.99 ± 0.02	-1.201 ± 0.032		-25.5 ± 0.2	0.1025 ± 0.39	
HNO ₃	29.32 ± 0.02	-0.955 ± 0.023		-71.6 ± 0.2	4.662 ± 0.32	
(CH ₃) ₄ NOH	85.54 ± 0.03	-1.609 ± 0.048		92.1 ± 0.5	-1.098 ± 1.0	
K ₂ SO ₄	32.41 ± 0.05	2.033 ± 0.21	-0.9415 ± 0.16	-256.7 ± 0.8	47.43 ± 10.9	-25.67 ± 14

^a The ± values are the statistical uncertainties (standard deviations) associated with the fit of eqn. (4) to our experimental results. Total uncertainties are larger than these ± values, as discussed in the text.

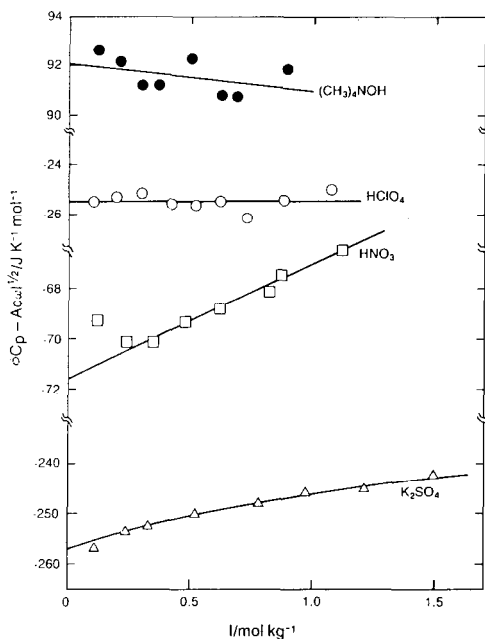


Fig. 2. ϕC_p minus the Debye-Hückel limiting slope ($A_C \omega I^{1/2}$) for aqueous HClO_4 , HNO_3 , $(\text{CH}_3)_4\text{NOH}$ and K_2SO_4 against I . Lines are least-squares fits of eqn. (4).

We have used $A_C = 32.783 \text{ J K}^{-1} \text{ kg}^{1/2} \text{ mol}^{-3/2}$ and $A_V = 1.8743 \text{ cm}^3 \text{ kg}^{1/2} \text{ mol}^{-3/2}$ [11,12].

Least-squares fits of equations of type (4) to our results in Table 1 lead to values of ϕC_p^\ominus , B_C , C_C , ϕV^\ominus , B_V and C_V that are listed in Table 2. To illustrate the quality of the fits of equations of type (4) to our results, we show graphs of type $\phi Y - A_Y \omega I^{1/2}$ against I in Figs. 1 and 2.

We estimate that the uncertainties in our ϕC_p^\ominus and ϕV^\ominus values for $(\text{CH}_3)_4\text{NOH}$ are $\pm 4 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$, respectively. These estimated uncertainties for aqueous HClO_4 and HNO_3 are $\pm 2 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$, with estimated uncertainties for aqueous K_2SO_4 intermediate between the values listed here for other electrolytes.

DISCUSSION

We can make both direct and indirect comparison of our results with results from earlier investigators, as follows.

Our $\phi V^\ominus(\text{HClO}_4)$ value of $43.99 \text{ cm}^3 \text{ mol}^{-1}$ is in excellent agreement with the value of $44.04 \text{ cm}^3 \text{ mol}^{-1}$ listed by Millero [13] and $44.097 \text{ cm}^3 \text{ mol}^{-1}$ reported by Herrington et al. [14] on the basis of their recent direct measurements. The average of these values is $\phi V^\ominus(\text{HClO}_4) = 44.04 \text{ cm}^3$

mol^{-1} , which we adopt as the best available value. The consistency of ${}^\phi V^\ominus$ values for several electrolytes is demonstrated by the reasonable agreement of this direct value with that of $44.2 \text{ cm}^3 \text{ mol}^{-1}$ calculated indirectly by Roux et al. [15].

The ${}^\phi C_p^\ominus(\text{HClO}_4)$ value of $-27.1 \text{ J K}^{-1} \text{ mol}^{-1}$ from Singh et al. [16], is in good agreement with our present $-25.5 \text{ J K}^{-1} \text{ mol}^{-1}$. Combination of ${}^\phi C_p^\ominus$ values for several electrolytes has led Roux et al. [15] to a corresponding $-25 \text{ J K}^{-1} \text{ mol}^{-1}$. We select ${}^\phi C_p^\ominus(\text{HClO}_4) = -25.5 \text{ J K}^{-1} \text{ mol}^{-1}$ as the best available value.

The ${}^\phi V^\ominus(\text{HNO}_3)$ value of $29.3 \text{ cm}^3 \text{ mol}^{-1}$ from direct measurements by Enea et al. [17] and the value of $29.5 \text{ cm}^3 \text{ mol}^{-1}$ calculated by Roux et al. [15] from ${}^\phi V^\ominus$ values for several electrolytes, together with $29.0 \text{ cm}^3 \text{ mol}^{-1}$ listed in Millero's tabulation [13] are in good agreement with our present ${}^\phi V^\ominus(\text{HNO}_3) = 29.32 \text{ cm}^3 \text{ mol}^{-1}$. Our selected value is ${}^\phi V^\ominus(\text{HNO}_3) = 29.3 \text{ cm}^3 \text{ mol}^{-1}$.

Our ${}^\phi C_p^\ominus(\text{HNO}_3) = -71.6$ is in excellent agreement with $-72.1 \text{ J K}^{-1} \text{ mol}^{-1}$ from direct measurements by Enea et al. [17] and with $-72 \text{ J K}^{-1} \text{ mol}^{-1}$ calculated by Roux et al. [15] from ${}^\phi C_p^\ominus$ values for several electrolytes. We select $-72 \text{ J K}^{-1} \text{ mol}^{-1}$ as the best available value.

For ${}^\phi V^\ominus(\text{K}_2\text{SO}_4)$ we have values from the literature [13,18,19] ranging from 30.1 to $32.8 \text{ cm}^3 \text{ mol}^{-1}$, along with our value ($32.41 \text{ cm}^3 \text{ mol}^{-1}$). Our weighted average of all these values is ${}^\phi V^\ominus(\text{K}_2\text{SO}_4) = 32.2 \text{ cm}^3 \text{ mol}^{-1}$.

Previous investigators [8,18,19] have reported ${}^\phi C_p^\ominus(\text{K}_2\text{SO}_4) = -251.0 \text{ J K}^{-1} \text{ mol}^{-1}$ and $-254.5 \text{ J K}^{-1} \text{ mol}^{-1}$. Our recalculations with their experimental results in combination with the revised [11,12] value of A_C and our present result leads to a selected ${}^\phi C_p^\ominus(\text{K}_2\text{SO}_4) = -256 \text{ J K}^{-1} \text{ mol}^{-1}$.

There have been no previous calorimetric or densimetric measurements on aqueous $(\text{CH}_3)_4\text{NOH}$, but measurements on solutions for tetramethylammonium halides have led to results that we can use of indirect comparisons. Volumetric data from Desnoyers and coworkers [20–22] and from Hepler et al. [23] for tetramethylammonium halides in combination with data for sodium halides and sodium hydroxide [8,15,24–27] lead to calculated values of ${}^\phi V^\ominus[(\text{CH}_3)_4\text{NOH}]$ from 85.3 to $85.6 \text{ cm}^3 \text{ mol}^{-1}$. On the basis of these values and our present result, we select ${}^\phi V^\ominus[(\text{CH}_3)_4\text{NOH}] = 85.5 \text{ cm}^3 \text{ mol}^{-1}$.

Heat capacities of solutions of the tetramethylammonium halides from Desnoyers and coworkers [8,21,22] in combination with heat capacities of solutions of sodium halides and sodium hydroxide [8,15,24–27] lead to values of ${}^\phi C_p^\ominus[(\text{CH}_3)_4\text{NOH}]$ from 94 to $98 \text{ J K}^{-1} \text{ mol}^{-1}$. Considerations of chemical problems lead us to believe that the lowest of these values is probably the best. On this basis and in consideration of our value ($92.1 \text{ J K}^{-1} \text{ mol}^{-1}$), we select ${}^\phi C_p^\ominus[(\text{CH}_3)_4\text{NOH}] = 94 \text{ J K}^{-1} \text{ mol}^{-1}$.

We now use our selected values of ${}^\phi C_p^\ominus$ and ${}^\phi V^\ominus$ for calculation of the very useful partial molar properties (standard state, infinite dilution) of ions

TABLE 3

Conventional [$\phi Y^\ominus(\text{H}^+) \equiv 0$] standard state partial molar volumes and heat capacities for aqueous ions at 298.15 K

Ion	ϕV^\ominus ($\text{cm}^3 \text{ mol}^{-1}$)	ϕC_p^\ominus ($\text{J K}^{-1} \text{ mol}^{-1}$)
ClO_4^-	44.04	-25.5
NO_3^-	29.3	-72
SO_4^{2-}	14.2	-282

based on the conventions that $\phi C_p^\ominus(\text{H}^+, \text{aq}) \equiv 0$ and $\phi V^\ominus(\text{H}^+, \text{aq}) \equiv 0$. Our selected values for the standard state partial molar properties of $\text{HClO}_4(\text{aq})$ and $\text{HNO}_3(\text{aq})$ lead directly to the desired conventional ϕC_p^\ominus and ϕV^\ominus for $\text{ClO}_4^- (\text{aq})$ and $\text{NO}_3^- (\text{aq})$, as listed in Table 3. Combination of $\phi V^\ominus(\text{K}^+) = 9.02 \text{ cm}^3 \text{ mol}^{-1}$ from Millero [13] with our previous ϕV^\ominus for aqueous K_2SO_4 leads to $\phi V^\ominus(\text{SO}_4^{2-}) = 14.2 \text{ cm}^3 \text{ mol}^{-1}$. Similarly, $\phi C_p^\ominus(\text{K}^+) = 13 \text{ J K}^{-1} \text{ mol}^{-1}$ from Roux et al. [15] leads to $\phi C_p^\ominus(\text{SO}_4^{2-}) = -282 \text{ J K}^{-1} \text{ mol}^{-1}$. The standard state partial molar properties of both $(\text{CH}_3)_4\text{N}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$ are defined more accurately by way of properties of electrolytes other than the $(\text{CH}_3)_4\text{NOH}(\text{aq})$ that we have investigated.

The standard state (infinite dilution) properties of aqueous electrolytes are additive, as illustrated by the calculations described in the preceding paragraph and also earlier in this paper. In contrast to this additivity, the parameters such as B_Y , that are used in the extended Debye-Hückel equation (eqn. (4)) to represent the properties of solutions at moderate ionic strengths, are not additive. The values of these parameters for $(\text{CH}_3)_4\text{NOH}(\text{aq})$ that we can calculate (by assuming additivity) from data for aqueous tetramethylammonium halides in combination with data for sodium halides and sodium hydroxide are not the same as the values obtained from our results, and listed here in Table 2. Calculations of this type provide a range of B_Y values (depending on the halide chosen) that are far outside our estimated uncertainties of these values. The direct B_Y values listed in Table 2 are the preferred values and are useful in ways that were mentioned in the second paragraph of this paper.

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