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APPARENT MOLAR HEAT CAPACITIES AND VOLUMES OF AQUEOUS ELECTROLYTES AT 25 °C: $NaIO_3$, $KMnO_4$, AND $MnCl_2$

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ABSTRACT

We have used a flow calorimeter and a flow densimeter for measurements leading to apparent molar heat capacities and apparent molar volumes of dilute aqueous solutions of $NaIO_3$, $KMnO_4$, and $MnCl_2$ at 25 °C. These apparent molar quantities have been extrapolated to infinite dilution to obtain the corresponding standard state apparent and partial molar heat capacities and volumes. which have then been used for the calculation of conventional ionic heat capacities and volumes.

INTRODUCTION

As part of our continuing program of measurements leading to thermal and volumetric properties of aqueous solutions, we have used a flow calorimeter and a flow densimeter for measurements on solutions of $NaIO_3$, $KMnO_4$, and $MnCl_2$. Results of these measurements have been used for calculation of apparent molar heat capcities and apparent molar volumes of all three electrolytes. Extrapolation of these apparent molar quantities to infinite dilution has yielded the standard state apparent molar (equal to partial molar) heat capacities and volumes that are of particular thermodynamic interest. Finally, these standard state quantities have been used for calculation of conventional ionic heat capacities and volumes.

EXPERIMENTAL

We have made heat capacity measurements on several electrolytes with two different Picker flow calorimeters of the same type, as previously described[1]. A small systematic error in the measurements with the first calorimeter has been identified and corrected[2, 3]. Tests by Picker and our comparisons[4–15] of results obtained with three new Picker calorimeters and one LKB calorimeter have confirmed that the

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earlier small error is negligible with the new calorimeter used for the measurements reported in this paper.

Densities of solutions have been measured with a flow densimeter[16].

Results of all our calorimetric and density measurements refer to 25.0 ± 0.1 °C.

Fisher certified $NaIO_3$ was recrystallized twice from doubly distilled water and then dried to constant weight at 105°C. Solutions were made by dissolving known masses of $NaIO_3$ in known masses of distilled water.

Two stock solutions were made with AR grade $KMnO_4$ (from B.D.H.) and distilled water. After storage in the dark for a few days, these stock solutions were filtered and then standardized by titration into sodium oxalate solution. Other solutions were prepared by dilution of these stock solutions.

Reagent grade $MnCl_2$ was recrystallized twice from dilute aqueous hydrochloric acid and then dissolved in distilled water to form a stock solution. This solution was standardized by titration with EDTA as described by Schwarzenbach and Flaschka[17]. Further solutions were prepared by dilution. Later, another stock solution was prepared, standardized, and diluted in the same way. Both stock solutions had pH $\cong$ 4.0. It is necessary that the pH be in this range for two reasons: (1) if the pH is too high, there is hydrolysis and possible air oxidation of Mn^{2+} (aq), and (2) if the pH is too low, the contribution of HCl to the properties of the solution is not negligible with respect to the contribution of $MnCl_2$.

RESULTS AND CALCULATIONS

Results of measurements with the Picker flow calorimeter are heat capacities per unit volume of solution. Combination of these heat capacities with the densities that we have also measured and the already known heat capacity of pure water permits the calculation of heat capacities expressed in terms of J K^{-1} (g of solution)$^{-1}$ and thence the desired apparent molar heat capacities that we represent by ϕ_C and express in terms of J K^{-1} $mole^{-1}$. Similarly, the densities of the solutions lead to the apparent molar volumes that we represent by ϕ_V and express in terms of cm^3 $mole^{-1}$. For both of these calculations, we have used equations of the type

$$\phi_Y = \frac{[Y(\text{soln.}) - n_1 Y_1^0]}{n_2} \tag{1}$$

in which Y is the extensive property (heat capacity or volume here) of a specified quantity of solution, n_1 is the number of moles of solvent in this specified quantity of solution, Y_1^0 is the property (heat capacity or volume) of one mole of pure solvent, and n_2 is the number of moles of solute in the specified quantity of solution.

Our experimental results have been used to obtain the apparent molar heat capacities and apparent molar volumes that are listed in Table 1. Heat capacities of solutions can be recovered from these tabulated ϕ_C values and corresponding molalities by way of

TABLE 1

APPARENT MOLAR HEAT CAPACITIES AND VOLUMES OF AQUEOUS ELECTROLYTES AT 25°C

m (mole kg^{-1}) KMnO$_4$	ϕ_C (J K^{-1} mole^{-1})	ϕ_V (cm^3 mole^{-1})	m (mole kg^{-1}) NaIO$_3$	ϕ_C (J K^{-1} mole^{-1})	ϕ_V (cm^3 mole^{-1})
0.04812	11.8	52.0	0.02873	−21.0	25.1
0.05530	11.8	51.9	0.04521	−16.7	25.2
0.06480	13.0	51.8	0.04959	−16.9	25.6
0.07582	14.7	52.1	0.06037	−13.1	25.5
0.09038	16.5	51.2*	0.06976	−12.0	25.6
0.10922	18.0	51.4*	0.08085	−9.1	25.6
0.12954	21.1	51.9	0.09045	−6.4	25.5
0.18278	26.6	52.2	0.09740	−5.1	26.3*
			0.13064	−0.7	25.7
MnCl$_2$			0.14614	+2.5	26.0
0.03954	−231.7	19.7			
0.05274	−227.3	20.3			
0.05862	−225.4	19.8			
0.07819	−220.9	20.4			
0.07916	−221.8	20.3			
0.10560	−216.5	20.6			
0.11739	−214.0	20.4			
0.13207	−211.4	20.7			
0.15665	−207.7	20.7			

* Not used in least squares fit.

$$c_p = \frac{[m\phi_C + 1000c_p^0]}{[1000 + mM_2]} \tag{2}$$

Similarly, densities of solutions can be recovered from the tabulated ϕ_V values and corresponding molalities by way of

$$d = \frac{[(1000 + mM_2)d_1^0]}{[1000 + md_1^0\phi_V]} \tag{3}$$

In these equations, c_p and c_p° are the heat capacities of solution and of pure water expressed in terms of J K^{-1} g^{-1}, m is the molality expressed in terms of (moles of solute) (kg of H$_2$O)$^{-1}$, M_2 is the molecular weight of solute, and d_1° is the density of pure water. We have used $c_p^\circ = 4.1793$ J K^{-1} mole^{-1} and $d_1^\circ = 0.997044$ g cm^{-3}.

Apparent molar properties of dilute solutions of strong electrolytes are accurately represented by equations of the form

$$\phi_Y = \phi_Y^0 + A_Y(d_1^0 m)^{\frac{1}{2}} + B_Y m \tag{4}$$

in which ϕ_Y° is the value of ϕ_Y at infinite dilution, A_Y is the limiting slope derived from the Debye–Hückel theory, m is the molality, and B_Y is an adjustable parameter. Our principal interest in this investigation has been in determining the ϕ_C° and ϕ_V° values

TABLE 2

PARAMETERS FOR EQN. (4)

Electrolyte	ϕ_C^0 *(J K^{-1} mole^{-1})*	B_C *(J K^{-1} mole^{-2} kg)*	ϕ_V *(cm^3 mole^{-1})*	B_V *(cm^3 mole^{-2} kg)*
$NaIO_3$	−29.6	148.0	24.8	2.7
$KMnO_4$	1.5	69.2	51.6	−1.3
$MnCl_2$	−259.3	−52.2	18.3	−8.6

TABLE 3

CONVENTIONAL [Based on $\phi_Y^0(H^+) = 0$] IONIC HEAT CAPACITIES AND VOLUMES FROM THIS INVESTIGATION

Ion	ϕ_C^0 *(J K^{-1} mole^{-1})*	ϕ_V^0 *(cm^3 mole^{-1})*
IO_3^-(aq)	−73	26.0
MnO_4^-(aq)	−12	42.6
Mn^{2+}(aq)	−5*	−17.4

* As discussed in the text, the best $\phi_C^0(Mn^{2+})$ is probably more negative than this value.

that are identical with the corresponding partial molar properties at infinite dilution ($\bar{C}_p^\circ$ and $\bar{V}^\circ$), both of which are of considerable thermodynamic importance. For our calculations leading to these values for aqueous $NaIO_3$ and $KMnO_4$, we have used $A_C(d_1^\circ)^{\frac{1}{2}} = 28.95$ J K^{-1} mole$^{-\frac{3}{2}}$ kg$^{\frac{1}{2}}$ and $A_V(d_1^\circ)^{\frac{1}{2}} = 1.865$ cm^3 mole$^{-\frac{3}{2}}$ kg$^{\frac{1}{2}}$, while for aqueous $MnCl_2$ we have used $A_C(d_1^\circ)^{\frac{1}{2}} = 150.4$ J K^{-1} mole$^{-\frac{3}{2}}$ kg$^{\frac{1}{2}}$ and $A_V(d_1^\circ)^{\frac{1}{2}} = 9.72$ cm^3 mole$^{-\frac{3}{2}}$ kg$^{\frac{1}{2}}$. Our ϕ_C°, B_C, ϕ_V°, and B_V values given in Table 2 are based on least squares fitting the results from Table 1 to equations of the type (4) with the appropriate limiting slopes cited above.

The most useful comparisons of the results we report here can be made by way of conventional ionic properties of ions based on $\phi_C^\circ(H^+) = 0$ and on $\phi_V^\circ(H^+) = 0$. For calculation of these conventional ionic properties for the ions of interest to us here, we make use of $\phi_C^\circ(Na^+) = 43$ J K^{-1} mole^{-1}, $\phi_C^\circ(K^+) = 13$ J K^{-1} mole^{-1}, and $\phi_C^\circ(Cl^-) = -127$ J K^{-1} mole^{-1} from Desnoyers et al.[3] and $\phi_V^\circ(Na^+) = -1.21$ cm^3 mole^{-1}, $\phi_V^\circ(K^+) = 9.02$ cm^3 mole^{-1}, and $\phi_V^\circ(Cl^-) = 17.83$ cm^3 mole^{-1} from Millero[18]. The resulting conventional ionic heat capacities and volumes are listed in Table 3.

The present investigation has led to $\phi_C^\circ = -29.6$ J K^{-1} mole^{-1} for aqueous $NaIO_3$, as compared with $\phi_C^\circ = -34.0$ J K^{-1} mole^{-1} from similar calorimetric measurements made at the Université de Sherbrooke[8]. Although the difference between these two values is small (less than the uncertainty in nearly all such values obtained before about 1970), we believe that the accuracy and especially the consistency of results of modern flow calorimetry are such that it may be possible to choose one or the other value as most likely to be the best. One way to approach this choice is by way of conventional ionic heat capacities for the aqueous iodate ion. Our present results lead to $\phi_C^\circ(IO_3^-) = -73$ J K^{-1} mole^{-1}, while the earlier measurements[8] on sodium iodate led to $\phi_C^\circ(IO_3^-) = -77$ J K^{-1} mole^{-1}. We now note that earlier measurements[8] in Lethbridge on aqueous potassium iodate solutions led to ϕ_C° for this salt and thence to $\phi_C^\circ(IO_3^-) = -72$ J K^{-1} mole^{-1}. The excellent agreement of this last value with our present results *suggests* that our present ϕ_C° for aqueous $NaIO_3$ is better than the earlier[8] value.

Present and past[8] ϕ_V° values for aqueous sodium iodate are in excellent agreement and our present $\phi_V^\circ(IO_3^-) = 26.0$ cm^3 mole^{-1} is in fair agreement with $\phi_V^\circ(IO_3^-) = 25.3$ cm^3 mole^{-1} selected by Millero[18] from results of several still earlier investigations.

We do not know of any prior heat capacity measurements that are related to the results we report here for aqueous potassium permanganate. Our $\phi_V^\circ = 51.6$ cm^3 mole^{-1} for this electrolyte leads to $\phi_V^\circ(MnO_4^-) = 42.6$ cm^3 mole^{-1}; these values can be compared with $\phi_V^\circ = 50.2$, 51.9, and 51.54 cm^3 mole^{-1} cited by Millero[18] for aqueous $KMnO_4$ and also with his selected $\phi_V^\circ(MnO_4^-) = 42.5$ cm^3 mole^{-1}.

Although we know of no heat capacity results for aqueous $MnCl_2$ to compare directly with our results, we can make some useful indirect comparisons by way of conventional ionic $\phi_C^\circ(Mn^{2+})$ values as follows. Our present results lead to $\phi_C^\circ(Mn^{2+}) = -5$ J K^{-1} mole^{-1}, while similar measurements on aqueous $Mn(ClO_4)_2$ (ref. 12) and $Mn(NO_3)_2$ (ref. 13) led to $\phi_C^\circ(Mn^{2+}) = -10$ and -12 J K^{-1} mole^{-1}, respectively. Again, the difference between these values is less than the uncertainties of nearly all standard state heat capacities determined before the last few years. But it should be noted that the discrepancy between the three $\phi_C^\circ(Mn^{2+})$ values cited above is larger than we have found in similar comparisons for any of the many other ions that we have investigated. We now suggest that the best $\phi_C^\circ(Mn^{2+})$ should be based largely on the earlier values from $Mn(ClO_4)_2$ and $Mn(NO_3)_2$ rather than on the present result for $MnCl_2$; this suggestion is based partly on the excellent agreement between the two earlier values and partly on the fact that we had greater experimental difficulties in preparing the $MnCl_2$ solutions than we had with the other Mn^{2+} solutions.

Our $\phi_V^\circ(Mn^{2+}) = -17.4$ cm^3 mole^{-1} is in excellent agreement with our previous[12, 13] $\phi_V^\circ(Mn^{2+}) = -17.3$ and -17.4 cm^3 mole^{-1}, which suggests that the best volume for this ion is slightly less negative than the $\phi_V^\circ(Mn^{2+}) = -17.7$ cm^3 mole^{-1} selected several years ago by Millero[18].

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