Review of the Apparent Molar Heat Capacities of NaCl(aq), HCl(aq), and NaOH(aq) and Their Representation Using the Pitzer Model at Temperatures from (298.15 to 493.15) K

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In this study, a new estimation of the standard state partial molar heat capacity (Cp^0) of three binary systems [NaCl(aq), HCl(aq), and NaOH(aq)] for temperatures ranging from (298.15 to 493.15) K is performed. From experimental data (available in the literature to date) corresponding to the apparent molar heat capacities of the above-mentioned electrolytes, a procedure based on the assumption of Pitzer's ion interaction model was applied to calculate these important Cp^0 values at a given temperature. Results obtained for each electrolyte (or ion) were correlated as functions of temperature by commonly used polynomial equations. Use of the hydrogen ion convention enabled estimates of the temperature-dependent values of Cp^0 of the individual ions Na^+(aq), Cl^-(aq), and OH^-(aq). When used to calculate the temperature-dependent values of the Gibbs free energy of formation of OH^-(aq), the formula for $Cp^0(T)$ of OH^-(aq) given herein provides good agreement with values derived from independent measurements of the ion constant of water at elevated temperatures. In the specific case of NaCl, a considerable disagreement was observed between the estimations performed using Archer's model (Archer, D. G. *J. Phys. Chem. Ref. Data* **1992**, 793−829) and some experimental data published years later. This fact can be explained, among other factors, by the dependence of the model parameters on the experimental uncertainty and systematic errors, which can be incurred during calorimetric experiments. For this reason, continuous revisions and updating of the proposed correlations are required when new experimental data become available.

Introduction

Knowledge of heat capacities of pure substances is critical to perform a wide variety of thermodynamic calculations, many of which involve the effects of changing temperature on other thermodynamic properties such as Gibbs energies and related equilibrium constants, enthalpies, and entropies.

In the present study, a new estimation of the standard state partial molar heat capacity (Cp^0) of three binary systems [NaCl(aq), HCl(aq), and NaOH(aq)] for temperatures ranging from (298.15 to 493.15) K is presented. The Pitzer ion-interaction model has been used to fit the previously published data concerning the apparent molar heat capacities for these aqueous electrolytes.

Assuming the hydrogen ion convention, which states that the conventional standard molar Gibbs energy of formation, entropy, and heat capacity of H^+ are all set equal to zero at all temperatures,[1] the standard state partial molar heat capacity of Na^+(aq), Cl^-(aq), and OH^-(aq) can be estimated from the apparent heat capacity values of the three analyzed electrolytes.

The main experimental data available in the literature for these solutions have been measured by means of mass-flow heat capacity calorimeters. In this type of instrument, convection heat transfer from the calorimetric tubing and the heater to the surroundings has been generally recognized as a principal source of systematic error in the measurements.[2] This experimental uncertainty motivates the performance of more reliable experimental studies which should be continuously collected and published. In addition, the mathematical procedures applied to the experimental data are gradually improving as a consequence of the use of more sophisticated algorithms and software applications. In our opinion, all of these reasons justify the development of the present study.

Table 1. Parameters of the Exponential Function Given by Equation 6

	temperature (K)				
	300	350	400	450	500
a_0	1.14073	1.03078	2.13600	2.61389	2.76623
a_1	2.75999	5.02168	7.14257	12.91512	29.51689
a_2	−0.00316	−0.00291	−0.00465	−0.00668	−0.00999
R^2adj	1.0000	0.9979	0.9999	0.9968	0.9985

Theoretical Background

The apparent molar heat capacity (Cp^ϕ) corresponds to the "excess" heat capacity (per mole of solute) with respect to the pure solvent of the solution. According to several researchers,[3−7] the apparent molar heat capacity (in J·mol^{-1}·K^{-1}) for binary systems can be written as a function of experimental heat capacity values as follows

$$Cp^\phi = MCp^{\exp} + \left[\frac{1000(Cp^{\exp} - Cp^0_{\mathrm{w}})}{m}\right] \tag{1}$$

where M is the molecular weight of the solute; m is the molality of the solution; $Cp^{\exp}$ is the specific heat capacity of the solution

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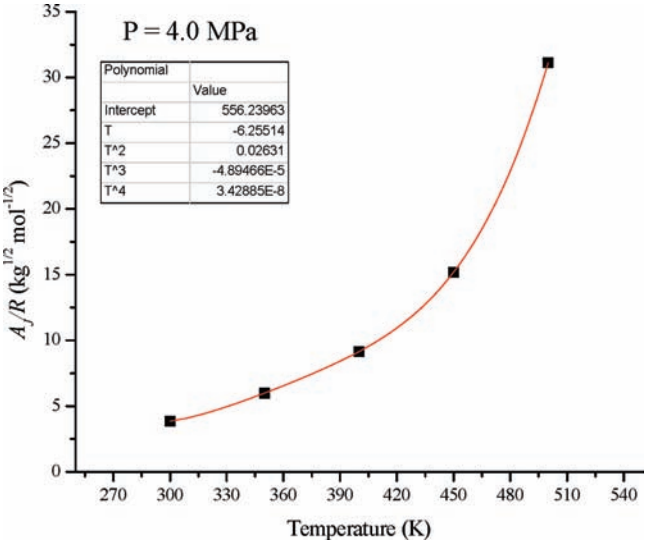

Polynomial	
	Value
Intercept	556.23963
T	-6.25514
T^2	0.02631
T^3	-4.89466E-5
T^4	3.42885E-8

Figure 1. A_J/R values as a function of temperature at a given pressure of 4.0 MPa.

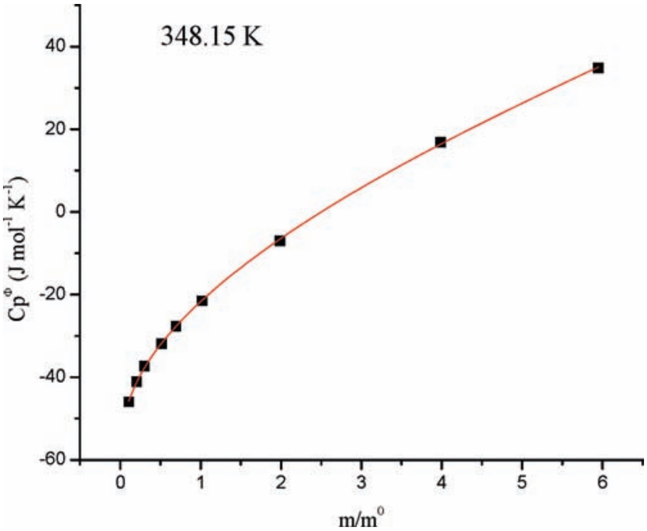

Figure 2. Apparent molar heat capacity of NaCl(aq) versus molality at 348.15 K (squares, experimental data from Saluja et al.;[4] line, Pitzer approach performed in this study).

(experimental value); and Cp^0_w is the specific heat capacity of pure water, respectively. It can be deduced from the second term in eq 1 that the precision and accuracy of Cp^{ϕ} is particularly sensitive to the difference ($Cp^{\text{exp}} - Cp^0_w$) and that this difference is amplified increasingly as m decreases because of the factor ($1/m$).

Pitzer's ion interaction approach[8] has been used with success to represent the properties of both single and multicomponent electrolyte solutions from low to high ionic strengths.[3] The basic equation of the ion interaction approach considers the excess free energy to be the sum of long-range electrostatic interactions (given by an extended Debye−Hückel theory) and specific short-range binary and ternary interactions between ions.[8] For heat capacities and for 1−1 electrolytes, Pitzer's formalism takes the following form

$$Cp^{\phi} = Cp^0 + v|z_M z_X| A_J (2b)^{-1} \ln(1 + bI^{1/2}) - 2v_M v_X R T^2 m \frac{[\beta^{(0)J}_{MX} + 2\beta^{(1)J}_{MX}[1 - (1 + \alpha I^{1/2})]\exp(-\alpha I^{1/2})]}{\alpha^2 I} - 2v_M v_X R T^2 m^2 C^J_{MX} \quad (2)$$

where v_M and v_X denote the stoichiometric coefficients of cations and anions, respectively ($v = v_M + v_X$); I is the molality-based ionic strength defined by eq 3; and z_i are the formal charges of the ions. The parameters α and b are arbitrary constants in the Pitzer equation and are assigned the values of (2.0 and 1.2) kg$^{1/2}$·mol$^{-1/2}$, respectively (for 1−1, 1−2, and 2−1 electrolytes).[4]

$$I = \frac{1}{2}\sum_i m_i z_i^2 \quad (3)$$

In eq 2, A_J (in J·kg$^{1/2}$·K^{-1}·mol$^{-3/2}$) is the molality-based Debye−Hückel coefficient for heat capacities. The value of this coefficient as a function of both temperature and pressure depends upon the dielectric constant and density of water. There are several published works in which the values of A_J are reported,[9,10] and they are in relatively good agreement (within 3 %).

It should be noted that α and b are assumed to be temperature independent. In this way, at fixed pressure and temperature, the apparent molar heat capacity is expressed in terms of four adjustable (temperature- and pressure-dependent) parameters per electrolyte, Cp^0, $\beta^{(0)J}_{MX}$, $\beta^{(1)J}_{MX}$, and C^J_{MX}, which are determined by fitting the equations to experimental Cp^{ϕ} data. The extrapolation of the model to infinite dilution corresponds to the parameter Cp^0 (the standard state partial molar heat capacity of the aqueous electrolyte).

As an alternative to the Pitzer approach, the more simplified Redlich−Rosenfeld−Meyer (RRM) type equation could be adequate for correlating experimental Cp^{ϕ} values up to an ionic strength of approximately 1 mol·kg^{-1}.[11] For heat capacities, the RRM model can be written as follows[12]

$$Cp^{\phi} = Cp^0 + (w)^{3/2} A_j^{1/2} (m)^{1/2} + B_C m \quad (4)$$

where w is a valence factor given by eq 5 and B_c is the only parameter fitted from the data and corresponds to an empirical coefficient which is a function of both pressure and temperature.

$$w = \frac{1}{2}(v_M z_M^2 + v_X z_X^2) \quad (5)$$

Procedure Description

In this section, the procedures which we employed to estimate the heat capacity values are described. Special attention is focused on the interpolation of the published values of the molality-based Debye−Hückel coefficient for heat capacities (A_J), the description of the nonlinear least-squares technique adopted to fit the experimental values of apparent molar heat capacity, and the statistical interpretation of the fitting results.

A_J Values. Recent values of the Debye−Hückel coefficients at selected temperatures and pressures were reported by Fernandez et al.[10] in 1997. Nevertheless, only values at (300, 350, 400, and 500) K and at (0.1, 10, 100, and 1000) MPa are available. This fact implies that, in most cases, the A_J value for a given temperature and pressure needs to be calculated according to the equations of Bradley and Pitzer.[9] The precision of this calculation can affect the reliability of the determined A_J value. Unfortunately, no details concerning the exact determination of A_J were reported in previous works (see, for instance, studies of Hovey et al.,[3] Saluja et al.,[4] and Magalhaes et al.[11]).

As an alternative to the direct (and arduous) calculation of A_J, we have developed an interpolation procedure to estimate the values of the Debye−Hückel coefficients from the data

Table 2. Sources of Experimental Data of Cp^{ϕ} of NaCl(aq)

		operating conditions		
reference	instrument	molality range	temperature range (K)	pressure (MPa)
Saluja et al. (1995)[4]	flow heat capacity microcalorimeter	0.1 to 6.0	298.15 to 371.82	0.60
Smith-Magowan and Wood (1981)[17]	heat flow calorimeter	0.1 to 3.0	320.55 to 497.73	10.00 to 17.70
Tanner and Lamb (1978)[18]	twin heat flow calorimeter	0.04 to 1.25	298.15 to 358.15	0.10
Perron et al. (1975)[19]	flow microcalorimeter	0.02 to 0.95	288.15 to 318.15	0.10

Table 3. Summarized Results for NaCl(aq) Using the Ion-Interaction (Pitzer) Approach

	T	p	Cp^0	$\beta_{MX}^{(0)J}$	$\beta_{MX}^{(1)J}$	C_{MX}^{J}		
source	(K)	(MPa)	($J \cdot mol^{-1} \cdot K^{-1}$)	($kg \cdot mol^{-1} \cdot K^{-2}$)	($kg^2 \cdot mol^{-2} \cdot K^{-2}$)	($kg^2 \cdot mol^{-2} \cdot K^{-2}$)	*Prob.* > *F*	R^2adj
Saluja et al. (1995)[4]	298.15	0.6	-86.22 ± 1.20	$-3.02\ 10^{-5} \pm 4.07 \cdot 10^{-6}$	$-4.51\ 10^{-5} \pm 1.35 \cdot 10^{-5}$	$2.49 \cdot 10^{-5} \pm 7.11 \cdot 10^{-6}$	$1.79 \cdot 10^{-9}$	0.9995
Saluja et al. (1995)[4]	323.15	0.6	-56.87 ± 0.59	$-5.09 \cdot 10^{-6} \pm 1.70 \cdot 10^{-6}$	$6.69 \cdot 10^{-6} \pm 5.66 \cdot 10^{-6}$	$-3.25 \cdot 10^{-6} \pm 2.97 \cdot 10^{-6}$	$4.24 \cdot 10^{-10}$	0.9998
Saluja et al. (1995)[4]	348.15	0.6	-59.25 ± 0.56	$-2.65 \cdot 10^{-6} \pm 1.39 \cdot 10^{-6}$	not significant	not significant	$3.95 \cdot 10^{-10}$	0.9998
Saluja et al. (1995)[4]	373.15	0.6	-76.13 ± 0.96	$-1.12 \cdot 10^{-5} \pm 2.41 \cdot 10^{-6}$	$-1.98 \cdot 10^{-5} \pm 8.00 \cdot 10^{-6}$	$1.06 \cdot 10^{-5} \pm 4.21 \cdot 10^{-6}$	$1.73 \cdot 10^{-9}$	0.9994
Tanner and Lamb (1978)[18]	298.15	0.1	-87.64 ± 1.38	$-2.58 \cdot 10^{-5} \pm 1.15 \cdot 10^{-5}$	not significant	not significant	$5.00 \cdot 10^{-15}$	0.9904
Tanner and Lamb (1978)[18]	318.15	0.1	-70.74 ± 1.33	$-4.27 \cdot 10^{-5} \pm 7.64 \cdot 10^{-6}$	$-1.79 \cdot 10^{-4} \pm 5.24 \cdot 10^{-5}$	$8.20 \cdot 10^{-5} \pm 2.26 \cdot 10^{-5}$	$3.60 \cdot 10^{-9}$	0.9955
Tanner and Lamb (1978)[18]	338.15	0.1	-59.08 ± 0.41	$-4.29 \cdot 10^{-6} \pm 2.00 \cdot 10^{-6}$	$-2.19 \cdot 10^{-5} \pm 1.32 \cdot 10^{-5}$	$7.87 \cdot 10^{-6} \pm 5.74 \cdot 10^{-6}$	$2.14 \cdot 10^{-7}$	0.9995
Tanner and Lamb (1978)[18]	358.15	0.1	-64.32 ± 6.42	not significant	not significant	not significant	$1.23 \cdot 10^{-3}$	0.9762
Smith-Magowan and Wood (1981)[17]	320.60	17.7	-43.84 ± 1.75	not significant	not significant	not significant	$2.58 \cdot 10^{-2}$	0.9970
Smith-Magowan and Wood (1981)[17]	358.40	17.7	-53.52 ± 3.39	not significant	not significant	not significant	$4.49 \cdot 10^{-2}$	0.9885
Smith-Magowan and Wood (1981)[17]	397.97	17.7	-83.12 ± 6.53	not significant	not significant	not significant	$5.04 \cdot 10^{-2}$	0.9750
Smith-Magowan and Wood (1981)[17]	452.56	17.7	-182.96 ± 14.24	$-4.17 \cdot 10^{-5} \pm 2.98 \cdot 10^{-5}$	$-1.53 \cdot 10^{-4} \pm 1.29 \cdot 10^{-4}$	$7.83 \cdot 10^{-5} \pm 6.52 \cdot 10^{-5}$	$5.16 \cdot 10^{-2}$	0.9645
Smith-Magowan and Wood (1981)[17]	491.05	17.7	-287.11 ± 3.15	$-5.08 \cdot 10^{-5} \pm 5.60 \cdot 10^{-6}$	$-1.98 \cdot 10^{-4} \pm 2.44 \cdot 10^{-5}$	$1.01 \cdot 10^{-4} \pm 1.22 \cdot 10^{-5}$	$7.22 \cdot 10^{-3}$	0.9991
Smith-Magowan and Wood (1981)[17]	497.73	17.7	-336.96 ± 21.57	$-6.62 \cdot 10^{-5} \pm 3.73 \cdot 10^{-5}$	$-2.41 \cdot 10^{-4} \pm 1.62 \cdot 10^{-4}$	$1.24 \cdot 10^{-4} \pm 8.17 \cdot 10^{-5}$	$4.27 \cdot 10^{-2}$	0.9731

reported by Fernandez and co-workers.[10] This procedure involves two stages. In the first one, the reported A_J values at constant temperature were fitted as a function of pressure by an exponential equation

$$\frac{A_J}{R} = a_0 + a_1 \exp(a_2 p) \qquad (6)$$

where p is the pressure (in MPa); R is the universal gas constant ($8.3145\ J \cdot mol^{-1} \cdot K^{-1}$); and a_0, a_1, and a_2 correspond to the adjustable parameters. This function type, which does not have a physical basis, was chosen among several mathematical expressions because it provides a reasonable representation of the behavior of the data. Table 1 shows the fitting results obtained for each temperature.

R^2adj corresponds to the adjusted regression coefficient (the coefficient of determination, R^2, adjusted by the degree of freedom[13]). In light of the results reported in Table 1, the agreement between data points and the exponential function was excellent.

The second stage of the interpolation procedure involves modeling of the A_J values at a given pressure value as a function of temperature. At any given pressure, the values of A_J/R at (300, 350, 400, 450, and 500) K are determined by the exponential equations (the parameters of which are reported in Table 1). Finally, these values of A_J/R at constant pressure were fitted by a polynomial function of fourth order in temperature. Using this procedure, we obtained excellent agreement between data points and the polynomial function for all cases involved in the present work. An example of this approach for a given pressure of 4.0 MPa is shown in Figure 1.

Least-Squares Curve Fitting. The experimental apparent heat capacity values at a given temperature and as a function of molality were fitted by the Pitzer model (see eq 2) using the Levenberg–Marquardt (L–M) algorithm.[14] The Origin Pro v. 8 software was used for this purpose. The goal of the fitting process is to estimate the parameter values which best describe the data. The standard way of finding the best fit is to choose the parameters that would minimize the deviations of the theoretical curve from the experimental points (chi-square minimization). As starting points of the iteration process, the Pitzer parameter values reported by Criss and Millero[15] for several aqueous electrolytes at 298.15 K were selected.

The solution given by the software was analyzed from a statistical point of view. Every fitting process was submitted to an F-test to check the ability of the model. The F-ratio quantifies the relationship between the relative increase in sum-of-squares and the relative increase in degrees of freedom. For a confidence interval of 95 %, probability values lower than 0.05 indicate that the null hypothesis can be rejected, and consequently, the model is significant. In addition, a t-test was also performed for each individual parameter (Cp^0, $\beta_{MX}^{(0)J}$, $\beta_{MX}^{(1)J}$, and C_{MX}^{J}) to assess its significance for a confidence interval of 95 %.

The results of the two tests and the R^2adj values should provide sufficient information about the ability of the Pitzer approach to fit the experimental data for each molality and temperature value.

Results and Discussion

In this section, the results obtained applying the Pitzer approach to previous published data sets for each electrolyte are presented.

NaCl(aq). Table 2 summarizes the experimental data sources for apparent molar heat capacities of NaCl(aq). All of the experiments were performed using flow calorimeters that have revolutionized the measurement of heat capacities of fluids. Nevertheless, concerns have been raised about the accuracy of this kind of calorimeter because of possible heat losses.[11] Several attempts have been made to quantify these losses (e.g., Desnoyers et al.[16]), but the results have been inconclusive.

The values of the apparent heat capacities reported by Saluja et al.[4] differ in a significant way from those calculated using the model of Archer[2] (differences ranging from 1.35 % at 298 K and $m = 0.1076$ to 17.29 % at 373 K and $m =$

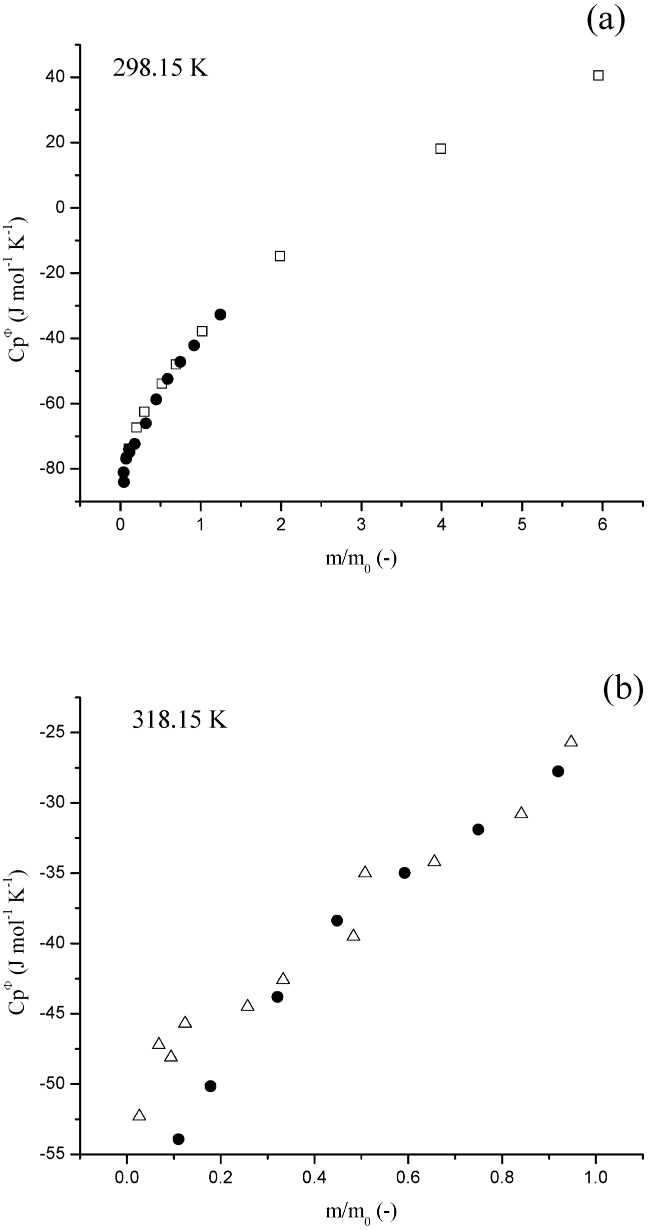

Figure 3. Apparent molar heat capacity of NaCl(aq) versus molality at (a) 298.15 K (□, experimental data from Saluja et al.;[4] ●, data from Tanner and Lamb[18]) and (b) 318.15 K (△, data from Perron et al.;[19] ●, data from Tanner and Lamb[18]).

Table 4. *Cp^0* Values of NaCl(aq) Estimated from the Low-Molality Experimental Data of Saluja et al.[4] and Their Comparison with Values Deduced from the Full Data Set Corresponding to the Same Work

T	Cp^0 values correlated from experimental low-molality data	difference with respect to the values reported in Table 3
(K)	(J·mol^{-1}·K^{-1})	(%)
298.15	−87.63 ± 0.54	−1.64
323.15	−56.00 ± 1.63	1.53
348.15	−60.26 ± 0.89	−1.70
373.15	−79.90 ± 2.23	−4.95

5.9477). Archer's model was developed in 1992 assuming a revised Pitzer equation (with more than 50 adjustable parameters) and fitting experimental results available at that time. Nevertheless, the more recent experimental data of Saluja and co-workers do not agree with Archer's model probably because of the excessive dependence of the adjusted parameters to the experimental uncertainty of data points evaluated by Archer.[2]

An example of application of the Pitzer model to fit a single given data set is presented in Figure 2 that displays the satisfactory fit of the Pitzer model to the apparent molar heat capacity as a function of molality for data reported by Saluja et al.[4] at 348.15 K.

A summary of the results obtained from the fitting process is given in Table 3. The data corresponding to the work of Perron and co-workers[19] are not reported in Table 3 as a consequence of the poor agreement between the Pitzer model and their experimental data. This fact could be due to the inaccuracy of the experimental measurements performed by Perron et al.[19] The last sentence is based on the comparison of the Cp^{ϕ} values obtained by Perron et al.[19] and Tanner and Lamb[18] at a temperature value of 318.15 K (see Figure 3b). This inconsistency between experimental data points from different sources is not present when data from Tanner and Lamb[18] and Saluja et al.[4] are compared (see Figure 3a). The parameters not reported correspond to the cases in which the *prob(t)* value obtained for each individual parameter was higher than 0.05 (not significant parameters assuming a confidence interval of 95 %). It is interesting to note that the model was significant in all cases. Only the results obtained from experiments reported by Smith-Magowan and Wood in 1981[17] exhibit *p*-values (*Prob.* > *F*) near 0.05.

It is well-known that the Pitzer model is adequate for correlating experimental Cp^{ϕ} values up to relatively high ionic strength values.[11] However, an additional estimation of the Pitzer parameters was performed using the experiments reported by Saluja et al.[4] and performed at relatively low molalities (up to 1 mol·kg^{-1}). Table 4 reports the results obtained for the Cp^0 parameter using only the low-molality data reported by Saluja and co-workers. The results obtained are relatively in agreement with the values reported in Table 3, and for this reason, the ability of the Pitzer model to correlate experimental NaCl data up to approximately 6 mol·kg^{-1} is reconfirmed here.

The ability of the alternative approach, the RRM type equation, has also been checked in this work for the apparent heat capacity values of the NaCl(aq) reported by Saluja et al.[4] at low molalities. The correlation results are given in Table 5. The RRM model seems to be appropriate in light of the correlating results shown in Table 5. This model can be an interesting option to obtain a preliminary Cp^0 value when the number of data points available is less than 5 (minimal data points required to perform a correlation by means of the Pitzer formalism).

Figure 4 shows the evolution of the Cp^0 values reported in Table 3 as a function of temperature. The apparent disagreement of the values calculated from the data of Smith-Magowan and Wood[17] could be due to both the relatively poor fit of the experimental data by the Pitzer model and the additional experimental uncertainty related to the operation at high pressures (see Table 2). The values displayed in Figure 4 were submitted to a fitting process using several polynomial functions assuming as negligible the pressure effects. This assumption may compromise the accuracy of the procedure. The effect of pressure on the apparent molar heat capacity can be expressed by the following equation

$$\left(\frac{\partial Cp^{\phi}}{\partial p}\right)_T = -T\left(\frac{\partial^2 V^{\phi}}{\partial T^2}\right)_p \tag{7}$$

The problem of solving this equation is the difficulty of determining second derivatives from experimental measure-

Table 5. Summarized Results for the NaCl(aq) Data Reported by Saluja and Coworkers[4] ($m \leq 1$ mol·kg^{-1}) Using the RRM Type Equation

T (K)	Cp^0 (J·mol^{-1}·K^{-1})	difference with respect to the values reported in Table 3 (%)	B_c (J·kg·mol^{-2}·K^{-1})	*Prob.* > *F*	R^2adj
298.15	−80.16 ± 1.67	−8.52	8.70 ± 0.66	$1.90 \cdot 10^{-8}$	0.9910
323.15	−59.19 ± 0.37	5.70	1.80 ± 0.15	$1.02 \cdot 10^{-11}$	0.9992
348.15	−63.46 ± 1.00	5.31	−2.97 ± 0.40	$1.36 \cdot 10^{-8}$	0.9932
373.15	−82.66 ± 1.23	3.45	−6.09 ± 0.49	$9.96 \cdot 10^{-9}$	0.9912

Table 6. Sources of Experimental Data of Cp^ϕ of HCl(aq)

reference	instrument	operating conditions: molality range	operating conditions: temperature range (K)	operating conditions: p (MPa)
Patterson et al. (2001)[27]	fixed-cell scanning calorimeter (NanoDSC model 6100, Calorimetry Sciences Corporation)	0.015 to 0.500	298.15 to 393.15	0.35
Sharigyn and Wood (1997)[30]	flow picker-type calorimeter	0.2 to 6.0	302.14 to 523.92	27.97
Tremaine et al. (1986)[28]	flow picker-type calorimeter	0.09 to 1.00	298.15 to 412.61	0.10 to 0.50
Allred and Wooley (1981)[29]	picker flow microcalorimeter	0.05 to 0.20	298.15 to 313.15	0.10

Table 7. Summarized Results for the HCl(aq) Using the Ion-Interaction (Pitzer) Approach

source	T (K)	p (MPa)	Cp^0 (J·mol^{-1}·K^{-1})	$\beta_{MX}^{(0)J}$ (kg mol^{-1}K^{-2})	$\beta_{MX}^{(1)J}$ (kg^2·mol^{-2}·K^{-2})	C_{MX}^J (kg^2·mol^{-2}·K^{-2})	*Prob.* > *F*	R^2*adj*
Patterson et al. (2001)[27]	298.15	0.35	−124.84 ± 1.58	$-4.55 \cdot 10^{-5} \pm 3.17 \cdot 10^{-5}$	$-7.72 \cdot 10^{-4} \pm 6.98 \cdot 10^{-4}$	not significant	$8.94 \cdot 10^{-5}$	0.9470
Patterson et al. (2001)[27]	303.15	0.35	−120.60 ± 1.70	$-4.77 \cdot 10^{-5} \pm 3.31 \cdot 10^{-5}$	not significant	not significant	$1.13 \cdot 10^{-4}$	0.9411
Patterson et al. (2001)[27]	308.15	0.35	−117.36 ± 1.57	$-4.40 \cdot 10^{-5} \pm 2.96 \cdot 10^{-5}$	not significant	$2.31 \cdot 10^{-4} \pm 2.07 \cdot 10^{-4}$	$1.02 \cdot 10^{-4}$	0.9510
Patterson et al. (2001)[27]	313.15	0.35	−114.79 ± 1.52	$-4.09 \cdot 10^{-5} \pm 2.78 \cdot 10^{-5}$	not significant	$2.16 \cdot 10^{-4} \pm 1.95 \cdot 10^{-5}$	$1.02 \cdot 10^{-4}$	0.9555
Patterson et al. (2001)[27]	318.15	0.35	−114.23 ± 1.61	$-4.53 \cdot 10^{-5} \pm 2.84 \cdot 10^{-5}$	$-7.89 \cdot 10^{-4} \pm 7.14 \cdot 10^{-4}$	$2.43 \cdot 10^{-4} \pm 1.99 \cdot 10^{-4}$	$1.16 \cdot 10^{-4}$	0.9558
Patterson et al. (2001)[27]	323.15	0.35	−113.88 ± 1.50	$-4.35 \cdot 10^{-5} \pm 2.58 \cdot 10^{-5}$	$-7.32 \cdot 10^{-4} \pm 6.48 \cdot 10^{-4}$	$2.27 \cdot 10^{-4} \pm 1.81 \cdot 10^{-4}$	$1.04 \cdot 10^{-4}$	0.9650
Patterson et al. (2001)[27]	328.15	0.35	−114.33 ± 1.60	$-4.64 \cdot 10^{-5} \pm 2.65 \cdot 10^{-5}$	$-7.83 \cdot 10^{-4} \pm 6.68 \cdot 10^{-4}$	$2.43 \cdot 10^{-4} \pm 1.86 \cdot 10^{-4}$	$1.18 \cdot 10^{-4}$	0.9646
Patterson et al. (2001)[27]	333.15	0.35	−114.26 ± 1.35	$-3.87 \cdot 10^{-5} \pm 2.18 \cdot 10^{-5}$	$-6.31 \cdot 10^{-4} \pm 5.48 \cdot 10^{-4}$	$1.98 \cdot 10^{-4} \pm 1.53 \cdot 10^{-4}$	$8.45 \cdot 10^{-5}$	0.9757
Patterson et al. (2001)[27]	338.15	0.35	−114.63 ± 1.09	$-3.20 \cdot 10^{-5} \pm 1.71 \cdot 10^{-5}$	$-4.94 \cdot 10^{-4} \pm 4.29 \cdot 10^{-4}$	not significant	$5.48 \cdot 10^{-5}$	0.9851
Patterson et al. (2001)[27]	343.15	0.35	−116.10 ± 1.15	$-3.18 \cdot 10^{-5} \pm 1.74 \cdot 10^{-5}$	$-4.71 \cdot 10^{-4} \pm 4.38 \cdot 10^{-4}$	$1.52 \cdot 10^{-4} \pm 1.22 \cdot 10^{-4}$	$5.96 \cdot 10^{-5}$	0.9852
Patterson et al. (2001)[27]	348.15	0.35	−117.26 ± 0.80	$-2.42 \cdot 10^{-5} \pm 1.18 \cdot 10^{-5}$	$-3.40 \cdot 10^{-4} \pm 2.96 \cdot 10^{-4}$	$1.11 \cdot 10^{-4} \pm 8.24 \cdot 10^{-5}$	$2.82 \cdot 10^{-5}$	0.9932
Patterson et al. (2001)[27]	353.15	0.35	−119.50 ± 0.94	$-2.68 \cdot 10^{-5} \pm 1.35 \cdot 10^{-5}$	$-3.75 \cdot 10^{-4} \pm 3.40 \cdot 10^{-4}$	$1.22 \cdot 10^{-4} \pm 9.48 \cdot 10^{-5}$	$3.85 \cdot 10^{-5}$	0.9915
Patterson et al. (2001)[27]	358.15	0.35	−121.93 ± 0.92	$-2.76 \cdot 10^{-5} \pm 1.28 \cdot 10^{-5}$	$-3.83 \cdot 10^{-4} \pm 3.21 \cdot 10^{-4}$	$1.25 \cdot 10^{-4} \pm 8.96 \cdot 10^{-5}$	$3.53 \cdot 10^{-5}$	0.9929
Patterson et al. (2001)[27]	363.15	0.35	−124.60 ± 0.95	$-2.80 \cdot 10^{-5} \pm 1.30 \cdot 10^{-5}$	$-3.86 \cdot 10^{-4} \pm 3.25 \cdot 10^{-4}$	$1.26 \cdot 10^{-4} \pm 9.08 \cdot 10^{-5}$	$3.70 \cdot 10^{-5}$	0.9930
Patterson et al. (2001)[27]	368.15	0.35	−127.86 ± 1.01	$-3.16 \cdot 10^{-5} \pm 1.34 \cdot 10^{-5}$	$-4.50 \cdot 10^{-4} \pm 3.36 \cdot 10^{-4}$	$1.45 \cdot 10^{-4} \pm 9.36 \cdot 10^{-5}$	$3.99 \cdot 10^{-5}$	0.9930
Patterson et al. (2001)[27]	373.15	0.35	−130.90 ± 0.89	$-3.04 \cdot 10^{-5} \pm 1.15 \cdot 10^{-5}$	$-4.20 \cdot 10^{-4} \pm 2.88 \cdot 10^{-4}$	$1.36 \cdot 10^{-4} \pm 8.04 \cdot 10^{-5}$	$2.98 \cdot 10^{-5}$	0.9951
*Pa*tterson et al. (2001)[27]	378.15	0.35	−135.14 ± 1.06	$-3.49 \cdot 10^{-5} \pm 1.33 \cdot 10^{-5}$	$-4.49 \cdot 10^{-4} \pm 3.33 \cdot 10^{-4}$	$1.60 \cdot 10^{-4} \pm 9.28 \cdot 10^{-5}$	$3.98 \cdot 10^{-5}$	0.9939
Patterson et al. (2001)[27]	383.15	0.35	−139.01 ± 1.07	$-3.66 \cdot 10^{-5} \pm 1.31 \cdot 10^{-5}$	$-5.23 \cdot 10^{-4} \pm 3.39 \cdot 10^{-4}$	$1.67 \cdot 10^{-4} \pm 9.18 \cdot 10^{-5}$	$3.90 \cdot 10^{-5}$	0.9944
Patterson et al. (2001)[27]	388.15	0.35	−143.55 ± 1.10	$-4.01 \cdot 10^{-5} \pm 1.31 \cdot 10^{-5}$	$-5.76 \cdot 10^{-4} \pm 3.28 \cdot 10^{-4}$	$1.84 \cdot 10^{-4} \pm 9.16 \cdot 10^{-5}$	$3.87 \cdot 10^{-5}$	0.9948
Patterson et al. (2001)[27]	393.15	0.35	−148.76 ± 1.29	$-4.59 \cdot 10^{-5} \pm 1.50 \cdot 10^{-5}$	$-6.98 \cdot 10^{-4} \pm 3.77 \cdot 10^{-4}$	$2.18 \cdot 10^{-4} \pm 1.05 \cdot 10^{-4}$	$5.05 \cdot 10^{-5}$	0.9936
Sharigyn and Wood (1997)[30]	302.14	27.97	−113.13 ± 2.39	$-9.10 \cdot 10^{-6} \pm 7.10 \cdot 10^{-6}$	$-2.51 \cdot 10^{-5} \pm 2.26 \cdot 10^{-5}$	not significant	$7.79 \cdot 10^{-3}$	0.9967
Sharigyn and Wood (1997)[30]	373.71	27.97	−118.02 ± 0.69	not significant	$6.03 \cdot 10^{-6} \pm 4.26 \cdot 10^{-6}$	$-3.24 \cdot 10^{-6} \pm 2.25 \cdot 10^{-6}$	$2.52 \cdot 10^{-3}$	0.9999
Sharigyn and Wood (1997)[30]	448.70	27.97	−206.34 ± 1.28	$-2.66 \cdot 10^{-5} \pm 2.05 \cdot 10^{-6}$	$-6.91 \cdot 10^{-5} \pm 6.77 \cdot 10^{-6}$	$3.68 \cdot 10^{-5} \pm 3.56 \cdot 10^{-6}$	$4.45 \cdot 10^{-5}$	0.9998
Sharigyn and Wood (1997)[30]	523.92	27.97	−377.11 ± 5.80	$-4.85 \cdot 10^{-5} \pm 6.79 \cdot 10^{-6}$	$-1.23 \cdot 10^{-4} \pm 2.24 \cdot 10^{-5}$	$6.59 \cdot 10^{-5} \pm 1.18 \cdot 10^{-5}$	$4.02 \cdot 10^{-4}$	0.9992
Tremaine et al. (1986)[28]	298.15	0.1	−127.03 ± 1.22	$-1.40 \cdot 10^{-5} \pm 8.09 \cdot 10^{-6}$	$-8.40 \cdot 10^{-5} \pm 6.44 \cdot 10^{-5}$	$3.57 \cdot 10^{-5} \pm 2.63 \cdot 10^{-5}$	$4.80 \cdot 10^{-10}$	0.9875
Tremaine et al. (1986)[28]	398.25	0.3	−130.02 ± 8.46	$3.18 \cdot 10^{-5} \pm 2.64 \cdot 10^{-6}$	$2.46 \cdot 10^{-4} \pm 1.85 \cdot 10^{-4}$	$-1.04 \cdot 10^{-4} \pm 7.80 \cdot 10^{-5}$	$4.07 \cdot 10^{-6}$	0.9733
Tremaine et al. (1986)[28]	412.61	0.5	−153.42 ± 2.32	not significant	$4.26 \cdot 10^{-5} \pm 6.36 \cdot 10^{-6}$	not significant	$6.14 \cdot 10^{-9}$	0.9951
Allred and Woolley (1981)[29]	298.15	0.1	−125.43 ± 1.22	$-4.19 \cdot 10^{-5} \pm 2.48 \cdot 10^{-5}$	$-9.94 \cdot 10^{-3} \pm 3.05 \cdot 10^{-3}$	$1.04 \cdot 10^{-3} \pm 4.14 \cdot 10^{-4}$	$9.54 \cdot 10^{-4}$	0.9970

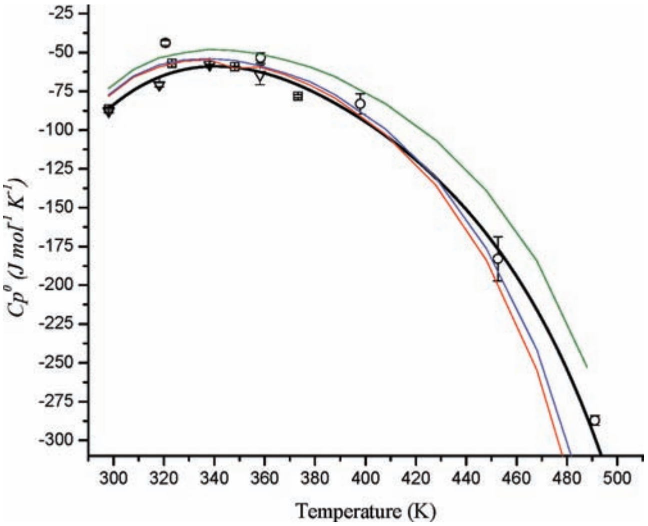

Figure 4. Estimated values of Cp^0 for NaCl(aq) using the Pitzer approach to correlate experimental Cp^ϕ values obtained by □, Saluja and co-workers;[4] ▽, Tanner and Lamb;[18] ○, and Smith-Magowan and Wood.[17] The black solid line corresponds to eq 8. The red, blue, and green solid lines correspond to the Cp^0 values estimated using the revised HKF model at 0.1 MPa, 4 MPa, and 17.7 MPa, respectively.

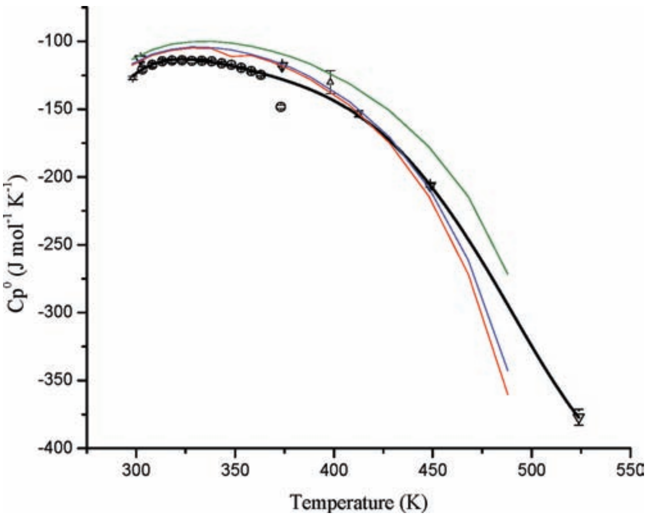

Figure 5. Estimated values of Cp^0 for HCl(aq) using the Pitzer approach to correlate experimental Cp^ϕ values obtained by ○, Patterson and co-workers;[27] ▽, Sharygin and Wood;[30] and △, Tremaine and co-workers.[28] The black solid line corresponds to eq 9. The red, blue, and green solid lines correspond to the Cp^0 values estimated using the revised HKF model at 0.1 MPa, 4 MPa, and 28 MPa, respectively.

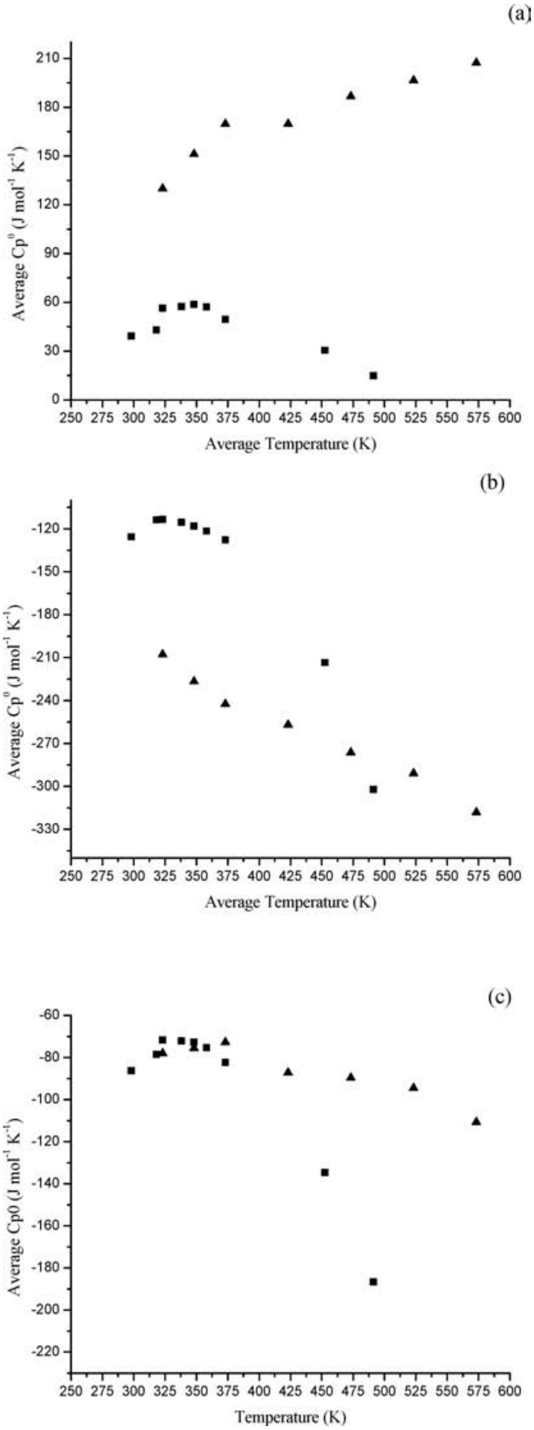

Figure 6. Average partial molar standard state heat capacity for aqueous (a) Na^+, (b) Cl^-, and (c) NaCl (■, values calculated in this work; ▲, values reported by Barner and Scheuerman[31]).

ments. From the literature, there are clearly large differences in precision of the volumetric data sets, as well as in data coverage of temperature, pressure, and concentration, and these proved to be troublesome in evaluating an overall fit of the volumetric data.[20] In addition to this, it should be kept in mind that one principal objective of estimating the standard state heat capacity (at a given temperature value) is the goal of calculating the heat capacity change for reactions involving aqueous ions. In this sense, Puigdomenech and co-workers[1] considered that pressure effects can be neglected for temperatures lower than 573 K.

From data displayed in Figure 4, the apparent best results (R^2adj = 0.9914) were obtained with the following equation

$$Cp^0(\mathrm{NaCl}) = -5.90873760962963 \cdot 10^4 + \frac{3.4028457831 \cdot 10^6}{T} + 3.764418314936 \cdot 10^2 T - 1.13798185529 T^2 + 1.6607597 \cdot 10^{-3} T^3 - 9.4980168897 \cdot 10^{-7} T^4 \quad (8)$$

The black solid line in Figure 4 corresponds to this equation. Obviously, the usefulness of eq 8 is limited to the applied temperature range. Extrapolations of this function will not provide reliable solutions. Figure 4 also shows the pressure-dependent Cp^0 values estimated using the revised Helgeson−Kirkham−Flowers (HKF) equations of state for aqueous species.[21−23] All of the calculations reported here (related to the revised HKF model) have been performed using the CHNOSZ software package (which can be freely downloaded from the project Web site at http://www.chnosz.net), which has been developed at U. C. Berkeley for the R software environment.[24] For the Cp^0 estimations made in the present study, the thermodynamic properties of pure water were calculated using an implementation in R code of the IAPWS-95 formulation.[25] The electrostatic properties of the pure solvent were calculated using the equations of Archer and Wang.[26]

Figure 4 indicates that the values calculated using the HKF model at 17.7 MPa agree reasonably well with the Cp^0 parameters obtained from the experimental data reported by Smith-Magowan and Wood[17] at the same pressure. This fact confirms the effect of the pressure on the value of standard state partial molar heat capacity. Nevertheless, it is also noted that eq 8 predicts in a reasonable way the Cp^0 values when the effect of pressure is not considered (when several data points measured at different pressures are combined). According to Puigdomenech and co-workers,[1] the measurement of aqueous solution heat capacities should be given a high priority, especially at high temperature, to validate the parameters of the equation of state based models.

HCl(aq). The same above-mentioned procedure was applied to estimate the temperature dependence of the standard state partial molar heat capacity values (Cp^0) for the aqueous hydrochloric acid system. Table 6 summarizes the experimental data sources for apparent molar heat capacities of HCl(aq). It is interesting to note that results reported by Patterson and co-workers[27] were obtained using a scanning calorimeter (not a

Table 8. Sources of Experimental Data of Cp^ϕ of NaOH(aq)

		operating conditions		
reference	instrument	molality range	temperature range (K)	pressure (MPa)
Magalhaes et al. (2002)[11]	picker flow calorimeter (Sodev, Canada)	0.02 to 1.00	298.15	0.10
Patterson et al. (2001)[27]	fixed-cell scanning calorimeter (NanoDSC model6100, Calorimetry Sciences Corporation)	0.015 to 0.500	298.15 to 393.15	0.35
Simonson et al. (1989)[33]	picker flow calorimeter	0.10 to 4.08	323.04 to 522.79	7.00
Conti et al. (1988)[34]	picker flow calorimeter	0.05 to 1.50	325.25 to 521.55	0.10 to 4.00
Allred and Wooley (1981)[29]	picker flow microcalorimeter	0.05 to 0.20	298.15 to 313.15	0.10

Table 9. Summarized Results for the Aqueous Electrolyte NaOH Using the Ion-Interaction (Pitzer) Approach

Source	T (K)	p (MPa)	Cp^0 ($\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$)	$\beta^{(0)J}_{\mathrm{MX}}$ ($\mathrm{kg \cdot mol^{-1} \cdot K^{-2}}$)	$\beta^{(1)J}_{\mathrm{MX}}$ ($\mathrm{kg^2 \cdot mol^{-2} \cdot K^{-2}}$)	C^J_{MX} ($\mathrm{kg^2 \cdot mol^{-2} \cdot K^{-2}}$)	*Prob.* > *F*	R^2adj
Magalhaes et al. (2002)[11]	298.15	0.1	-99.12 ± 0.44	$-3.68 \cdot 10^{-5} \pm 4.84 \cdot 10^{-6}$	not significant	not significant	$7.08 \cdot 10^{-14}$	0.9995
Patterson et al. (2001)[27]	298.15	0.35	-102.42 ± 1.41	$-6.33 \cdot 10^{-5} \pm 2.73 \cdot 10^{-5}$	$-6.55 \cdot 10^{-4} \pm 6.33 \cdot 10^{-4}$	$1.96 \cdot 10^{-4} \pm 1.80 \cdot 10^{-5}$	$1.42 \cdot 10^{-4}$	0.9912
Patterson et al. (2001)[27]	303.15	0.35	-88.86 ± 1.35	$-5.20 \cdot 10^{-5} \pm 2.53 \cdot 10^{-5}$	not significant	not significant	$1.78 \cdot 10^{-4}$	0.9904
Patterson et al. (2001)[27]	308.15	0.35	-78.49 ± 1.29	$-4.44 \cdot 10^{-5} \pm 2.35 \cdot 10^{-5}$	not significant	not significant	$2.18 \cdot 10^{-4}$	0.9902
Patterson et al. (2001)[27]	313.15	0.35	-69.80 ± 1.25	$-3.67 \cdot 10^{-5} \pm 2.20 \cdot 10^{-5}$	not significant	not significant	$2.69 \cdot 10^{-4}$	0.9897
Patterson et al. (2001)[27]	318.15	0.35	-63.30 ± 1.18	$-3.08 \cdot 10^{-5} \pm 2.01 \cdot 10^{-5}$	not significant	not significant	$3.04 \cdot 10^{-4}$	0.9904
Patterson et al. (2001)[27]	323.15	0.35	-58.13 ± 1.16	$-2.60 \cdot 10^{-5} \pm 1.91 \cdot 10^{-5}$	not significant	not significant	$3.62 \cdot 10^{-4}$	0.9904
Patterson et al. (2001)[27]	328.15	0.35	-54.19 ± 1.06	$-2.10 \cdot 10^{-5} \pm 1.69 \cdot 10^{-5}$	not significant	not significant	$3.64 \cdot 10^{-4}$	0.9919
Patterson et al. (2001)[27]	333.15	0.35	-51.13 ± 0.98	$-1.62 \cdot 10^{-5} \pm 1.51 \cdot 10^{-5}$	not significant	not significant	$3.62 \cdot 10^{-4}$	0.9931
Patterson et al. (2001)[27]	338.15	0.35	-49.22 ± 1.03	$-1.57 \cdot 10^{-5} \pm 1.55 \cdot 10^{-5}$	not significant	not significant	$4.53 \cdot 10^{-4}$	0.9924
Patterson et al. (2001)[27]	343.15	0.35	-48.22 ± 1.01	$-1.48 \cdot 10^{-5} \pm 1.47 \cdot 10^{-5}$	$-1.05 \cdot 10^{-4} \pm 3.42 \cdot 10^{-5}$	not significant	$4.73 \cdot 10^{-4}$	0.9930
Patterson et al. (2001)[27]	348.15	0.35	-47.83 ± 1.08	$-1.30 \cdot 10^{-5} \pm 1.18 \cdot 10^{-5}$	$-8.27 \cdot 10^{-5} \pm 3.57 \cdot 10^{-5}$	$2.24 \cdot 10^{-5} \pm 1.16 \cdot 10^{-5}$	$5.72 \cdot 10^{-4}$	0.9921
Patterson et al. (2001)[27]	353.15	0.35	-47.93 ± 0.96	not significant	$-3.56 \cdot 10^{-5} \pm 3.09 \cdot 10^{-5}$	not significant	$4.58 \cdot 10^{-4}$	0.9940
Patterson et al. (2001)[27]	358.15	0.35	-48.51 ± 0.95	not significant	$4.68 \cdot 10^{-5} \pm 2.96 \cdot 10^{-5}$	not significant	$4.35 \cdot 10^{-4}$	0.9944
Patterson et al. (2001)[27]	363.15	0.35	-49.93 ± 0.91	not significant	$5.95 \cdot 10^{-5} \pm 5.74 \cdot 10^{-5}$	$-2.14 \cdot 10^{-5} \pm 7.79 \cdot 10^{-6}$	$3.74 \cdot 10^{-4}$	0.9952
Patterson et al. (2001)[27]	368.15	0.35	-52.08 ± 0.92	not significant	$1.11 \cdot 10^{-4} \pm 2.71 \cdot 10^{-5}$	$-3.50 \cdot 10^{-5} \pm 7.70 \cdot 10^{-6}$	$3.53 \cdot 10^{-4}$	0.9954
Patterson et al. (2001)[27]	363.15	0.35	-49.93 ± 0.91	not significant	$5.95 \cdot 10^{-5} \pm 5.74 \cdot 10^{-5}$	$-2.14 \cdot 10^{-5} \pm 7.80 \cdot 10^{-6}$	$3.74 \cdot 10^{-4}$	0.9952
Patterson et al. (2001)[27]	368.15	0.35	-52.08 ± 0.92	not significant	$1.11 \cdot 10^{-4} \pm 2.71 \cdot 10^{-5}$	$-3.50 \cdot 10^{-5} \pm 7.70 \cdot 10^{-6}$	$3.53 \cdot 10^{-4}$	0.9954
Patterson et al. (2001)[27]	373.15	0.35	-54.70 ± 0.91	not significant	$1.01 \cdot 10^{-4} \pm 2.62 \cdot 10^{-5}$	$-3.28 \cdot 10^{-5} \pm 7.44 \cdot 10^{-6}$	$3.12 \cdot 10^{-4}$	0.9958
Patterson et al. (2001)[27]	378.15	0.35	-57.70 ± 0.81	not significant	$1.61 \cdot 10^{-4} \pm 2.26 \cdot 10^{-5}$	$-5.02 \cdot 10^{-5} \pm 4.45 \cdot 10^{-5}$	$2.17 \cdot 10^{-4}$	0.9969
Patterson et al. (2001)[27]	383.15	0.35	-61.17 ± 0.72	not significant	$1.79 \cdot 10^{-4} \pm 1.75 \cdot 10^{-4}$	not significant	$1.49 \cdot 10^{-4}$	0.9978
Patterson et al. (2001)[27]	388.15	0.35	-65.17 ± 0.62	not significant	$1.81 \cdot 10^{-4} \pm 1.65 \cdot 10^{-4}$	$-5.66 \cdot 10^{-5} \pm 4.71 \cdot 10^{-5}$	$9.76 \cdot 10^{-5}$	0.9984
Patterson et al. (2001)[27]	393.15	0.35	-68.41 ± 0.42	$1.13 \cdot 10^{-5} \pm 4.65 \cdot 10^{-6}$	$3.71 \cdot 10^{-4} \pm 1.08 \cdot 10^{-4}$	$-1.14 \cdot 10^{-4} \pm 3.06 \cdot 10^{-5}$	$3.81 \cdot 10^{-5}$	0.9993
Simonson et al. (1989)[33]	323.04	7.00	-59.91 ± 1.20	$-3.32 \cdot 10^{-5} \pm 3.80 \cdot 10^{-6}$	$-5.99 \cdot 10^{-5} \pm 1.32 \cdot 10^{-5}$	$3.30 \cdot 10^{-5} \pm 6.88 \cdot 10^{-6}$	$4.49 \cdot 10^{-4}$	0.9994
Simonson et al. (1989)[33]	373.07	7.00	-46.92 ± 1.66	$-8.40 \cdot 10^{-6} \pm 3.92 \cdot 10^{-6}$	not significant	not significant	$1.44 \cdot 10^{-3}$	0.9982
Simonson et al. (1989)[33]	423.09	7.00	-96.32 ± 6.89	not significant	$3.77 \cdot 10^{-5} \pm 3.44 \cdot 10^{-5}$	not significant	$7.13 \cdot 10^{-3}$	0.9892
Simonson et al. (1989)[33]	522.79	7.00	-449.63 ± 23.87	$-1.75 \cdot 10^{-5} \pm 1.71 \cdot 10^{-5}$	$-9.23 \cdot 10^{-5} \pm 9.07 \cdot 10^{-5}$	not significant	$2.95 \cdot 10^{-3}$	0.9719
Conti et al. (1988)[34]	325.25	0.10	$-64.43 \pm \cdot 10.69$	$-6.12 \cdot 10^{-5} \pm 5.88 \cdot 10^{-5}$	$-2.47 \cdot 10^{-4} \pm 3.66 \cdot 10^{-5}$	not significant	$1.55 \cdot 10^{-2}$	0.8124
Conti et al. (1988)[34]	373.97	0.12	-46.10 ± 5.12	not significant	$-1.35 \cdot 10^{-5} \pm 1.33 \cdot 10^{-5}$	not significant	$6.30 \cdot 10^{-3}$	0.9371
Conti et al. (1988)[34]	422.45	0.50	-85.78 ± 3.20	$2.42 \cdot 10^{-5} \pm 1.04 \cdot 10^{-5}$	$1.75 \cdot 10^{-4} \pm 6.49 \cdot 10^{-5}$	$-7.92 \cdot 10^{-5} \pm 2.92 \cdot 10^{-5}$	$1.22 \cdot 10^{-4}$	0.9882
Conti et al. (1988)[34]	470.55	1.50	-182.85 ± 4.72	not significant	$3.52 \cdot 10^{-5} \pm 7.73 \cdot 10^{-6}$	not significant	$3.51 \cdot 10^{-5}$	0.9893
Conti et al. (1988)[34]	521.55	4.00	-436.03 ± 11.67	not significant	$4.50 \cdot 10^{-5} \pm 1.55 \cdot 10^{-6}$	not significant	$3.65 \cdot 10^{-5}$	0.9865
Allred and Woolley (1981)[29]	298.15	0.1	-95.16 ± 4.56	$-3.12 \cdot 10^{-4} \pm 1.42 \cdot 10^{-4}$	$-2.35 \cdot 10^{-2} \pm 1.55 \cdot 10^{-2}$	$3.65 \cdot 10^{-3} \pm 2.15 \cdot 10^{-3}$	$1.54 \cdot 10^{-7}$	0.9850
Allred and Woolley (1981)[29]	313.15	0.1	-57.86 ± 5.04	not significant	$7.13 \cdot 10^{-3} \pm 1.20 \cdot 10^{-3}$	not significant	$1.54 \cdot 10^{-7}$	0.9850

flow calorimeter). The results of the fitting process using the Pitzer model are reported in Table 7. Some results obtained from the data published by Tremaine et al.[28] and Allred and Woolley[29] are not reported in Table 7 as a consequence of the bad fitting results obtained. The experimental uncertainty could be higher in the data reported in relatively old studies because of the systematic errors that have been identified in subsequent studies.[2,11]

The results reported in Table 7 concerning the standard-state heat capacity values (Cp^0) are displayed in Figure 5. We must remark that results obtained from Patterson and co-workers[27] are in relatively good agreement with those obtained from other researchers who used Picker flow calorimeters. The values displayed in Figure 5 were submitted to a fitting process using several polynomial functions assuming as negligible the pressure effects. The best results (R^2adj = 0.9986) were obtained using the following equation

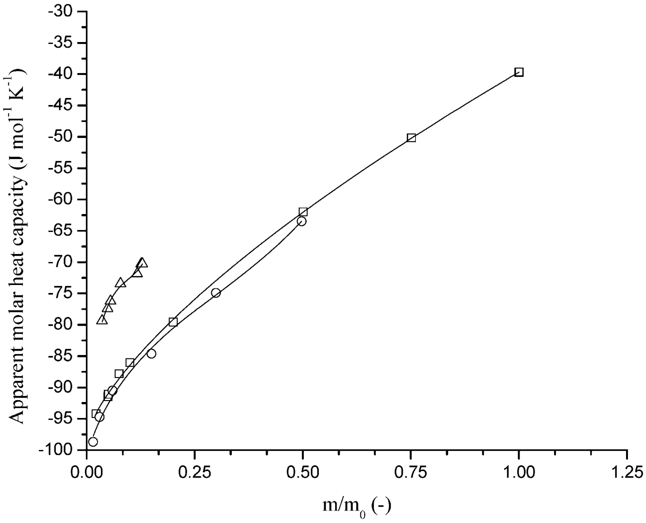

Figure 7. Apparent molar heat capacity of NaOH(aq) versus molality at 298.15 K (□, experimental data from Magalhaes et al.;[11] ○, data from Patterson et al.;[27] Δ, data from Allred and Woolley;[29] solid lines, Pitzer model for each data set using parameters reported in Table 9).

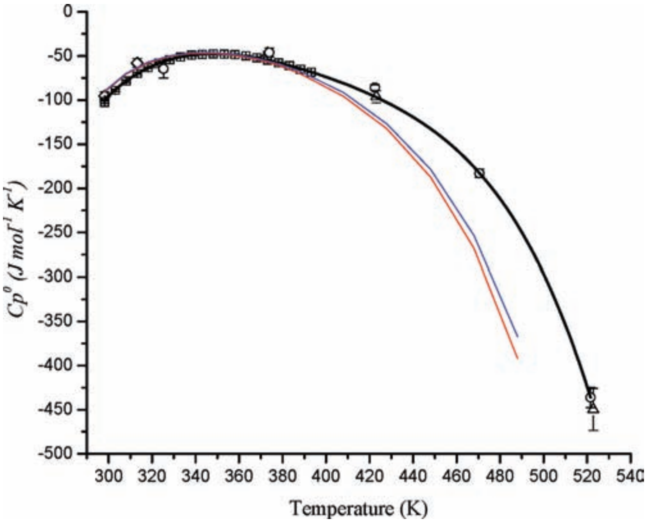

Figure 8. Estimated values of Cp^0 for NaOH(aq) using the Pitzer approach to correlate experimental Cp^ϕ values obtained by □, Patterson and co-workers;[27] △, Simonson and co-workers;[33] ○, Conti and co-workers;[34] ◇, Allred and Woolley;[29] ▽, and Magalhaes and co-workers..[11] The black solid line corresponds to eq 13. The red and blue solid lines correspond to the Cp^0 values estimated using the revised HKF model at (0.1 and 4) MPa, respectively.

$$Cp^0(\mathrm{HCl}) = 1.773367390171106 \cdot 10^5 - \frac{1.375818326510^{-7}}{T} - 9.097252470855 \cdot 10^2 T + 2.3157483398 T^2 - 2.9169397 \cdot 10^{-3} T^3 + 1.4503729301 \cdot 10^{-6} T^4 \quad (9)$$

The black solid line in Figure 5 corresponds to eq 9. In this case, the revised HKF model values depart from the corresponding Cp^0 values obtained from the experimental data reported by Sharygin and Wood[30] at 28 MPa. This fact emphasizes the need for additional experimental data to refine the current HKF parameters.

At this point, the standard-state heat capacity of individual ions (Na^+ and Cl^-) at a given temperature can be calculated assuming the hydrogen ion convention

$$Cp^0(\mathrm{Cl}^-) = Cp^0(\mathrm{HCl}) \quad (10)$$

$$Cp^0(\mathrm{Na}^+) = Cp^0(\mathrm{NaCl}) - Cp^0(\mathrm{Cl}^-) \quad (11)$$

The values calculated from eq 11 were then fitted by means of eq 12 with a relatively high degree of precision (R^2adj = 0.9210; $R^2 = 0.9895$).

$$Cp^0(\mathrm{Na}^+) = -5.428997123294567 \cdot 10^5 + \frac{4.023267891510^{-7}}{T} + 2.9012416922429 \cdot 10^3 T - 7.67288559593 T^2 + 1.00449709 \cdot 10^{-2} T^3 - 5.2095477204 \cdot 10^{-6} T^4 \quad (12)$$

It is interesting to compare the average Cp^0 values (average value between the Cp^0 at 298.15 K and the Cp^0 at a given temperature value) calculated using eqs 10 and 11 with those reported by Barner and Scheuerman[31] and determined assuming the "entropy correspondence principle" enunciated by Criss and Cobble.[32] These authors observed that the "absolute" entropies of many aqueous ions at elevated temperatures could be correlated with their "absolute" entropies at 298.15 K, provided that the entropy of H^+(aq) could be assigned a temperature-dependent, nonzero "absolute" reference value. Figure 6 shows this comparison for both Na^+(aq) and Cl^-(aq) ions. The large differences observed for the average heat capacity values for individual ions could be due, among other factors, to the inherent assumptions of the two approaches: the "hydrogen ion convention" assumed in the present work and the "entropy correspondence principle" adopted by Criss and Cobble.[32] The relatively good agreement observed for the aqueous NaCl electrolyte at low temperatures could be an indicator that the differences for individual ions can be explained by the assumption of different conventions. Nevertheless, the larger disagreement observed when the temperature increases could be related to the fact that the approach developed by Criss and Cobble is less accurate at temperatures higher than approximately 400 K.

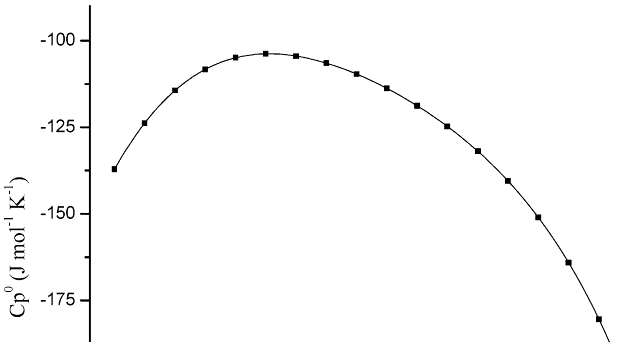

Figure 9. Estimated values of Cp^0 for the aqueous OH^- ion (■, calculated values from eq 14; solid line, eq 15).

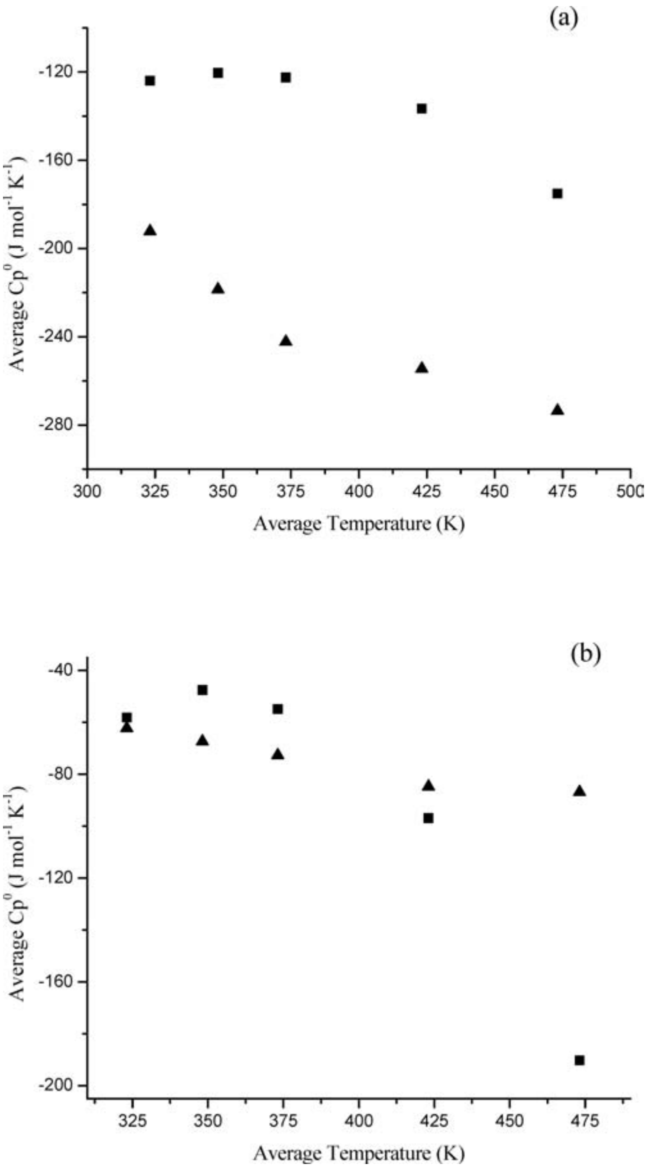

Figure 10. Average partial molar standard-state heat capacity for aqueous (a) OH^- and (b) NaOH (■, values calculated in this work; ▲, values reported by Barner and Scheuerman[31]).

NaOH(aq). For the aqueous NaOH electrolyte, Table 8 summarizes the experimental data sources for apparent molar heat capacities which have been considered in this work. Table 9 reports the results obtained for the Pitzer model parameters.

The apparent heat capacities at 298.15 K reported by Magalhaes et al.,[11] Patterson et al.,[27] and Allred and Woolley[29] are compared in Figure 7. Results obtained by Allred and Woolley are clearly in disagreement with those reported by other authors. This fact could be explained by the higher systematic errors inherent to the calorimetric measurements performed by Allred and Woolley in 1981. As has been mentioned above, the accuracy of a Picker flow calorimeter depends to a great extent on the correct quantification of the heat losses. It is reasonable to think that this correction process has been improved in recent years, and for this reason, the most recent experiments could provide the most reliable results. In any case, the standard-state partial molar heat capacity (Cp^0) reported in Table 9 and calculated from the data set reported by Allred and Woolley[29] ($-95.16\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$) is not in serious disagreement with the same parameter estimated from the data of Magalhaes et al.[11] ($-99.12\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$).

In addition, Figure 7 also shows that the data published by Patterson et al.[27] and experimentally obtained using a fixed-cell scanning calorimeter (equipped with a constant-volume cell) are in excellent agreement with those reported by Magalhaes et al.[11] This fact could confirm the ability of this type of calorimeter to provide reliable heat capacity results for electrolyte solutions. However, the calorimeter used by Patterson and co-workers was calibrated[35] assuming the values reported by Archer[2] for the aqueous NaCl electrolyte and estimated from experimental data obtained using Picker flow calorimeters. Unfortunately, no additional calibrations with other liquid standards (as suggested by Cerdeirina et al.[36]) were performed to check the accuracy of the instrument. For this reason, we believe that the high similarity between the results obtained from the two types of calorimeters is expected.

The results reported in Table 9 concerning the standard state heat capacity values (Cp^0) for the aqueous NaOH electrolyte are displayed in Figure 8. The black solid line in the figure corresponds to the fitted curve according to eq 13. The fit quality was excellent ($R^2\mathrm{adj} = 0.9999$).

$$Cp^0(\mathrm{NaOH}) = -4.19505400752324 \cdot 10^4 + \frac{1.9615565652 \cdot 10^6}{T} + 2.959385831059 \cdot 10^2 T - 0.95475222715 T^2 + 1.4644429 \cdot 10^{-3} T^3 - 8.7369274529 \cdot 10^{-7} T^4 \tag{13}$$

From analyzing Figure 8, it can be deduced that, at temperatures higher than 400 K, the revised HKF model values significantly depart from the corresponding Cp^0 values.

The standard state heat capacity of the individual aqueous $\mathrm{OH^-}$ ion as a function of temperature can be calculated assuming the hydrogen ion convention and the heat capacity values for $\mathrm{Na^+(aq)}$ estimated in the present study

$$Cp^0(\mathrm{OH^-}) = Cp^0(\mathrm{NaOH}) - Cp^0(\mathrm{Na^+}) \tag{14}$$

The results provided by eq 14 are displayed in Figure 9. The evolution of the Cp^0 values as a function of temperature can be reproduced by the following equation ($R^2\mathrm{adj} = 1.0000$)

$$Cp^0(\mathrm{OH^-}) = -3.79062897306247 \cdot 10^4 + \frac{2.0095760617 \cdot 10^6}{T} + 2.539848770523 \cdot 10^2 T - 0.80251271175 T^2 + 1.22030464 \cdot 10^{-3} T^3 - 7.306388889 \cdot 10^{-7} T^4 \tag{15}$$

The comparison between the average Cp^0 values estimated here and those reported by Barner and Scheuerman[31] has also been performed for both $\mathrm{OH^-(aq)}$ and NaOH(aq). Figure 10 shows how the comparative trends are similar to those obtained for aqueous NaCl electrolyte: a significant disagreement is observed for the individual ion Cp^0 values (probably as a consequence of the different reference values adopted by the two procedures), and a relatively good agreement (but only at low temperatures) is observed for the electrolyte results.

Water Ionization. The ionization constant of water (K_W) is a benchmark property in aqueous solution chemistry and has been experimentally obtained over wide ranges of temperature and pressure. On the basis of these available experimental measurements, several authors have developed models to predict the pK_w value as a function of both temperature and density.[37−41] Recently, Bandura and Lvov[42] reported a new model (based on a semitheoretical approach in which statistical thermodynamics is employed) to successfully fit the experimental data. From these pK_w values, we can estimate the $\Delta_\mathrm{f}G^0$ value for $\mathrm{OH^-(aq)}$ at a given temperature, according to the following relationship

$$\Delta_\mathrm{f}G^0_{\mathrm{OH^-}} = -RT \ln K_\mathrm{w} + \Delta_\mathrm{f}G^0_{\mathrm{H_2O}} \tag{16}$$

with $\Delta_\mathrm{f}G^0_{\mathrm{H^+}} \equiv 0$ (hydrogen ion convention) and $\Delta_\mathrm{f}G^0_{\mathrm{H_2O}}$ being given by Wagner and Pruss.[25]

On the other hand, the $\Delta_\mathrm{f}G^0_{\mathrm{OH^-}}$ values can also be estimated according to the second-law extrapolation

$$\Delta_\mathrm{r}G^0(T) = \Delta_\mathrm{r}G^0(298.15) - (T - 298.15)\Delta_\mathrm{r}S^0(298.15) + \int_{298.15}^{T} \Delta_\mathrm{r}C_p^0 \mathrm{d}T - T\int_{298.15}^{T} \frac{\Delta_\mathrm{r}C_p^0}{T}\mathrm{d}T \tag{17}$$

$$\Delta_\mathrm{f}G^0_{\mathrm{OH^-}}(T) = \Delta_\mathrm{r}G^0(T) - \Delta_\mathrm{f}G^0_{\mathrm{H_2O}}(T) \tag{18}$$

Equation 17 can be rewritten assuming an average value of $\Delta_\mathrm{r}C_p^0$ for the range of 298.15−T

$$\Delta_\mathrm{r}G^0(T) = \Delta_\mathrm{r}G^0(298.15) - (T - 298.15)\Delta_\mathrm{r}S^0(298.15) + \Delta_\mathrm{r}C_p^0\left[T - 298.15 - T\ln\left(\frac{T}{298.15}\right)\right] \tag{19}$$

A way to check the reliability of the above-reported Cp^0 values for $\mathrm{OH^-(aq)}$ is to compare the temperature-dependent values of $\Delta_\mathrm{f}G^0_{\mathrm{OH^-}}$ calculated from (a) eq 16 using the pK_w values reported by Bandura and Lvov,[42] (b) eq 17 or 19 and eq 18 using the Cp^0 values for $\mathrm{OH^-(aq)}$ provided by eq 15, and (c) eqs 18 and 19 using the average heat capacities reported by Barner and Scheuerman.[31] The data corresponding to the Cp^0 values for the ordinary water have been obtained from the IAPWS-95 formulation[25] at 0.1 MPa and saturation pressure (for temperatures higher than 273.15 K). Table 10 summarizes the results of the comparison process and shows the good agreement of $\Delta_\mathrm{f}G^0_{\mathrm{OH^-}}$ given by Barner and Scheuerman with those calculated from the ionization constant of water reported by Bandura and Lvov. Likewise, values of $\Delta_\mathrm{f}G^0_{\mathrm{OH^-}}$ calculated using eqs 18 and 19 with Cp^0 values for $\mathrm{OH^-(aq)}$ provided by eq 15 agree well with those calculated from the ionization constant of water reported by Bandura and Lvov, whereas the use of the integral form (eq 17) offers poor agreement above

Table 10. Values of $\Delta_\mathrm{f}G^0_{\mathrm{OH^-}}$ at Various Temperatures at 0.1 MPa (T < 273.15 K) or Saturation Pressure (T > 273.15 K)

	$\Delta_\mathrm{f}G^0_{\mathrm{OH^-}}$ ($\mathrm{kJ \cdot mol^{-1}}$)			
temperature (K)	using pK_w values reported in ref 42 and eq 15	using heat capacity data from the present work and eqs 18 and 17	Using heat capacity data from the present work and eqs 16 and 17	Using heat capacity data from ref 31 and eqs 18 and 17
323.15	−156.20	−157.13	−157.30	−157.15
348.15	−149.92	−150.87	−151.53	−150.93
373.15	−143.42	−144.26	−145.72	−144.36
423.15	−129.44	−129.84	−134.86	−130.29
473.15	−114.44	−112.88	−122.86	−114.94

Table 11. Standard Molar Heat Capacity Change (in $J\cdot mol^{-1}\cdot K^{-1}$) for the Ionization of Water at 10 MPa

temperature (K)	323.15	348.15	373.15	423.15	473.15
this study from equilibrium: $H_2O = H^+ + OH^-$	−185.90	−178.96	−183.48	−213.09	−293.27
this study from equilibrium: $NaOH + HCl = NaCl + H_2O$	−187.02	−180.63	−180.17	−203.87	−298.27
difference (%)	0.60	0.93	−1.80	−4.33	1.71
ref 43	−186 ± 5	n.a.	−182 ± 5	−224 ± 10	−314 ± 26
revised HKF model	−175.25	−170.47	−179.21	−229.63	−355.20

373 K. Special attention should be focused on analyzing these unexpected discrepancies in future studies.

In addition to this, we can also estimate the standard (infinite dilution) molar heat capacity change for the ionization of water, $\Delta_r C_p^0$, from the standard partial molar heat capacities of NaCl(aq), NaOH(aq), and HCl(aq) (given by eqs 8, 9, and 13, respectively) by assuming electrolyte additivity

$$\text{NaOH(aq)} + \text{HCl(aq)} = \text{NaCl(aq)} + \text{H}_2\text{O} \qquad \text{(I)}$$

$$\Delta_r C_p^0(T) = C_{p\text{NaOH(aq)}}^0(T) + C_{p\text{HCl(aq)}}^0(T) - C_{p\text{NaCl(aq)}}^0(T) - C_{p\text{H}_2\text{O}}^0(T) \qquad (20)$$

The data corresponding to the Cp^0 values for the ordinary water have been obtained from the IAPWS-95 formulation[25] at 10 MPa. Table 11 reports the results of these calculations and shows the relatively good agreement between the $\Delta_r C_p^0$ values calculated from the two equilibrium approaches. This fact seems to confirm the accuracy of estimations of Cp^0 for all of the electrolytes analyzed here. Table 11 also shows that results obtained from the present study are in agreement (especially at temperatures below 373.15 K) with those recently reported by Schrödle and co-workers.[43] Exact agreement at higher temperatures would not be expected because of the uncertainties that inevitably arise from the different procedures used in the extrapolation to infinite dilution. In addition to this, the results obtained for the $\Delta_r C_p^0$ values by using the revised HKF equations show a significant disagreement with the values obtained using eqs 8, 9, 13, and 20 (see Table 11). This discrepancy increases at high temperatures as the differences among Cp^0 predicted values increase, especially for HCl(aq) and NaOH(aq) (see Figures 5 and 8).

Conclusions

In the present work, the experimental data available in the literature corresponding to the apparent molar heat capacity, Cp^ϕ, of three aqueous electrolytes (NaCl, HCl, and NaOH) were fitted using Pitzer's ion-interaction model. As a result of this mathematical approach, the standard state heat capacity values have been estimated as a function of temperature for each electrolyte.

The new estimated Cp^0 values for both molecules and ions have been correlated as a function of temperature (from 298.15 K to approximately 493.15 K) by means of relatively simple equations (assuming the pressure effects as negligible). The use of these mathematical expressions can be very useful to perform thermodynamic calculations involving temperature changes.

In addition, the average Cp^0 values estimated in the present study for NaCl(aq) and NaOH(aq) are clearly in disagreement (especially at temperatures higher than 400 K) with those calculated assuming the ion "absolute" entropy values reported by Barner and Scheuerman in 1973. In our opinion, this finding is very important because many thermodynamic studies were based on the assumption of the values available in Barner and Scheuerman's handbook. Further comparative analyses would be interesting to confirm this observed trend.

In the specific case of NaCl, a significant disagreement was observed between experimental data reported by Saluja and co-workers[4] in 1995 and the estimations performed using Archer's model[2] (in which the parameters were adjusted from experimental data points reported before 1992). This fact can be related, among other factors, to the critical dependence of the model parameters on the experimental uncertainty. For this reason, continuous updates of the proposed models are required when new experimental data become available. The experimental uncertainty is related to the systematic errors that can be introduced during the calorimetric measurements. In this sense, it would be interesting to perform further studies using both flow and differential scanning calorimeters to gain a better understanding of the peculiarities of each type of instrument. Probably the performance of a round robin study for a given pure liquid substance will be needed in the near future.

On the other hand, further studies focused on evaluating and overall fit of volumetric data are also needed \to determine the pressure effects on the standard-state heat capacities and, consequently, to improve the accuracy of the heat capacity predictions as a function of temperature.

Additional thermodynamic calculations, based on the ionization of water, were performed to check the accuracy of the new Cp^0 values. The good agreement of $\Delta_f G^0_{OH^-}$ values with those calculated from the ionization constant of water reported by Bandura and Lvov[42] corroborates the usefulness of eq 15 to estimate the temperature-dependent Cp^0 values for the OH^-(aq) ion. Also, a comparison of estimated $\Delta_r C_p^0$ values, which represent two different equilibrium approaches (the ionization of water and the NaOH/HCl neutralization), shows satisfactory agreement. This last fact gives credence to the validity and reliability of the estimations of the standard state molar heat capacities of NaOH(aq), HCl(aq), and NaCl(aq) made in this paper.

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Appendix

Nomenclature

A_J	molality-based Debye−Hückel coefficient for heat capacities ($J\cdot kg^{1/2}\cdot K^{-1}\cdot mol^{-3/2}$)
B_c	adjustable parameter of the RRM model ($J\cdot kg\cdot mol^{-1}\cdot K^{-1}$)
b	arbitrary constant of the Pitzer equation ($1.2\ kg^{1/2}\cdot mol^{1/2}$)
Cp^0	Standard-state partial molar heat capacity ($J\cdot mol^{-1}\cdot K^{-1}$)
Cp^ϕ	apparent molar heat capacity ($J\cdot mol^{-1}\cdot K^{-1}$)
Cp^{exp}	specific heat capacity of the solution ($J\cdot g^{-1}\cdot K^{-1}$)
$Cp^0{}_w$	specific heat capacity of water ($J\cdot g^{-1}\cdot K^{-1}$)
C_{MX}^J	ion interaction parameter for Pitzer's equation

I	molality-based ionic strength ($mol\cdot kg^{-1}$ for 1−1 electrolytes)
K_w	Ionization constant of water (−)
M	molecular weight of the solute ($g\cdot mol^{-1}$)
m	molality of the solute ($mol\cdot kg^{-1}$)
m^0	molality value at the reference state (1.0 $mol\cdot kg^{-1}$)
p	pressure (MPa)
R	universal gas constant (8.3145 $J\cdot mol^{-1}\cdot K^{-1}$)
R^2	coefficient of determination
R^2adj	adjusted regression coefficient
T	temperature (K)
V^ϕ	apparent partial molar volume ($cm^3\cdot mol^{-1}$)
w	valence factor used in the RRM equation
z	formal charge of an ion

Greek Symbols

α	arbitrary constant of the Pitzer equation (2.0 $kg^{1/2}\cdot mol^{1/2}$)
$\beta_{MX}^{(0)J}$, $\beta_{MX}^{(1)J}$	ion interaction parameters for Pitzer's equation
$\Delta_f G^0$	standard-state Gibbs free energy of formation ($J\cdot mol^{-1}$)
$\Delta_r G^0$	standard-state Gibbs free energy of reaction ($J\cdot mol^{-1}$)
$\Delta_r S^0$	standard-state entropy change for the reaction ($J\cdot mol^{-1}\cdot K^{-1}$)
$\Delta_r C_p^0$	standard-state heat capacity change for the reaction ($J\cdot mol^{-1}\cdot K^{-1}$)
υ_M	stoichiometric coefficients of a cation
υ_X	stoichiometric coefficients of an anion

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