

Densities of NaCl(aq) to the temperature 523 K at pressures to 40 MPa measured with a new vibrating-tube densitometer^a

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Relative densities of NaCl(aq) with molalities m : $0.165 \leq m/(\text{mol} \cdot \text{kg}^{-1}) \leq 5.484$ have been measured with a vibrating-tube densitometer between the temperatures 298 K and 523 K at pressures of 7 MPa and 40 MPa. These results span the pressure and temperature ranges of several earlier volumetric studies of NaCl(aq) and extend to higher molalities than have been reported previously. The densities are in good agreement with published values through $T = 523$ K. Apparent molar volumes V_{ϕ} calculated from the measured density differences have been fitted with the Pitzer ion-interaction treatment, with appropriate expressions chosen for the temperature and pressure dependence of the molality-independent parameters of the model. It was found that the partial molar volume at infinite dilution V_{ϕ}^{∞} and second- and third-virial parameters $\beta^{(0)V}$ and C^V were sufficient to represent V_{ϕ} at nearly the estimated experimental uncertainty.

1. Introduction

This paper is the second⁽¹⁾ in a series in which we report new volumetric measurements for binary and ternary aqueous solutions containing NaCl and CaCl₂ at temperatures from 298 K to 623 K and pressures from 0.1 MPa to 40 MPa. The range of conditions over which measurements have been made encompasses those encountered in natural and technological systems including geothermal reservoirs and power plants, oil reservoirs, steam generator devices, and other geologic and industrial environments. These volumetric properties, in addition to their intrinsic interest, permit calculation of the pressure dependence of thermodynamic properties of solutions, leading to improved representations of mineral and solid solubilities over wide ranges of temperature and pressure. In the present study, relative densities

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of NaCl(aq) were measured using a new vibrating-tube densitometer at temperatures T from 298 K to 523 K, along isobars at pressures p near 7 MPa and 40 MPa, and for molalities m ranging from $0.165 \text{ mol} \cdot \text{kg}^{-1}$ to $5.484 \text{ mol} \cdot \text{kg}^{-1}$. Apparent molar volumes V_ϕ calculated from the measured relative densities have been represented with a pressure- and temperature-dependent form of the Pitzer ion-interaction treatment, and the resulting equation was used to calculate V_ϕ at conditions appropriate for detailed comparison with the wide selection of published results for NaCl(aq).

Although published reports of the volumetric properties of NaCl(aq) at $T > 298 \text{ K}$ and $p > 0.1 \text{ MPa}$ are relatively plentiful,⁽²⁻¹⁰⁾ most of the measurements have been limited to $T \leq 475 \text{ K}$, $p \leq 2 \text{ MPa}$, and $m \leq 4.5 \text{ mol} \cdot \text{kg}^{-1}$. Exceptions include the measurements by Hilbert,⁽⁴⁾ by Grant-Taylor,⁽⁵⁾ and by Majer *et al.*^(9,10) Hilbert's measurements are of limited precision and number and are widely spaced at $p \leq 40 \text{ MPa}$ and $T \leq 523 \text{ K}$. Most of the results of Majer *et al.*^(9,10) are limited to $m \leq 3.1 \text{ mol} \cdot \text{kg}^{-1}$ at $T \geq 470 \text{ K}$, and the work of Grant-Taylor is limited to $p = 20 \text{ MPa}$ and $m \leq 4 \text{ mol} \cdot \text{kg}^{-1}$ at $T \leq 623 \text{ K}$.

Two extensive reviews of the thermodynamic properties of NaCl(aq), including volumetric properties spanning the ranges of conditions investigated in this work, have been published. The work of Rogers and Pitzer⁽¹¹⁾ modeled volumetric properties of NaCl(aq) within the framework of the Pitzer ion-interaction treatment; this study provided the expressions for volumetric properties used by Pitzer *et al.*⁽¹²⁾ in their complete description of NaCl(aq) thermodynamics to $T = 573.15 \text{ K}$ and $p = 100 \text{ MPa}$. Recently, Archer⁽¹³⁾ reanalyzed the experimental results for this system; his extended ion-interaction treatment, which includes an assumed dependence of the second virial parameter on ionic strength, may be used to calculate thermodynamic properties for these solutions through $T = 598.15 \text{ K}$ at pressures to 100 MPa. While the Pitzer ion-interaction formalism is used here to represent the results of this study, it is not intended to supersede the work of Rogers and Pitzer⁽¹¹⁾ or of Archer.⁽¹³⁾ Instead, this study provides new experimental measurements at conditions which have received relatively little attention in earlier work, and presents extensive comparisons of available values of V_ϕ . A comprehensive critical analysis of the volumetric properties of NaCl(aq) will be made when additional measurements at higher temperatures have been completed.

2. Experimental

All values reported here were obtained as density differences $\delta\rho$ between NaCl(aq) and an appropriate reference fluid, here chosen to be water, using vibrating-tube densitometers at Oak Ridge National Laboratory (ORNL). At $T = 298.15 \text{ K}$, $\delta\rho$ was measured with a Paar DMA 60 and 512 HP remote cell with a stainless-steel tube. The densitometer tube in this case was insulated by a stainless-steel jacket through which thermostatted (ethene glycol + water) was circulated. The temperature of the tube was monitored with a calibrated 100Ω platinum resistance thermometer (RTD) located between the inner sleeve of the insulating jacket and the vibrating-tube. Temperature was maintained at $(298.15 \pm 0.1) \text{ K}$. The apparatus used to maintain

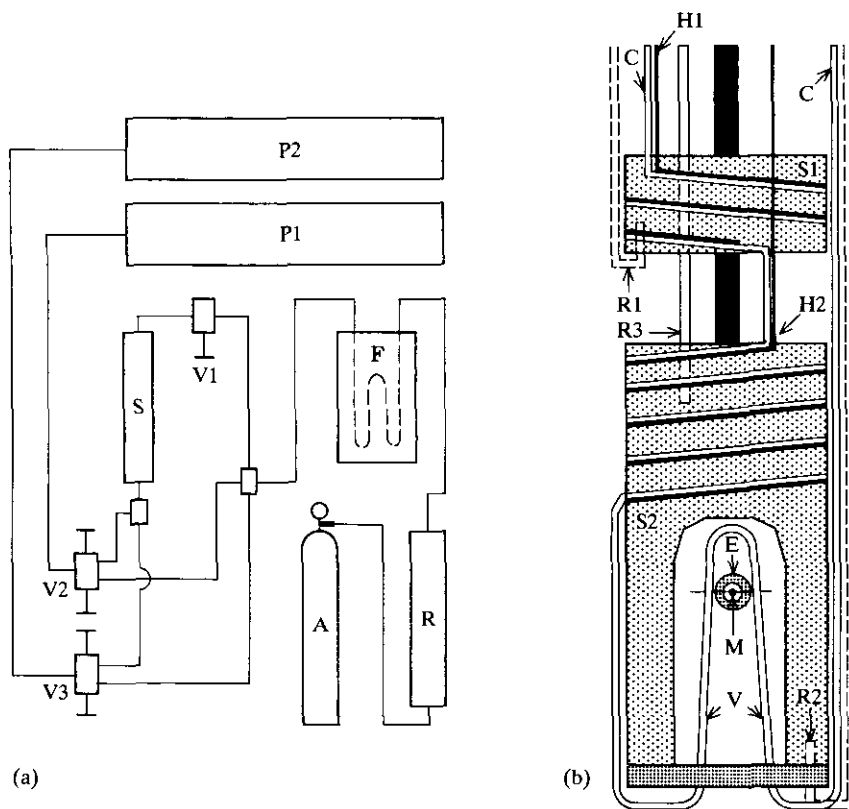


FIGURE 1. (a) Simplified schematic diagram of the densitometer and fluid-delivery system, and (b) details of the vibrating-tube densitometer assembly. Labels are referenced in the text.

pressure and deliver salt solution to the vibrating-tube was the same as described below.

For $T \geq 323$ K, measurements of $\delta\rho$ were made using a vibrating-tube densitometer constructed by the senior author at ORNL. The principal components of the densitometer assembly are shown in figure 1. The body of the assembly consisted of two silver blocks S1 and S2 each of which was coaxially wound with electrical heating coils H1 and H2 and Hastelloy C-276 capillary-tubing C (1.1 mm i.d., 1.6 mm o.d.). Approximate temperature control was maintained with a tube furnace (Marshall Furnace Co.) in which the densitometer assembly was suspended; the heating coils were used as low-power trim heaters to supplement the tube furnace and provide more precise temperature control. Coil H1 preheated the solution and held the temperature of block S1 at 1 K to 3 K above the experimental temperature maintained by coil H2 on block S2.

At the bottom of the block S2 the capillary tube was bent into an inverted U-shape which entered the cavity within the block and was clamped to it at its base. This 10 cm portion of the tube above the clamp formed the vibrating tube V. An

Alnico-V permanent magnet M was mounted on the vibrating tube near its apex normal to the plane of the tube. The poles of the magnet passed through two wire-coil electromagnets E wound with alumina-insulated silver wire (Secor Metals) on Macor ceramic forms (Aremco, Inc.) and mounted with ceramic cement (Aremco Cerabond 569) on opposite sides of the lower silver block. The electromagnets were connected through impedance-matching transformers (with a 25-to-1 turn ratio) to the Paar 512 HP sensing and drive circuits. The period τ of vibration of the vibrating tube was determined by measuring the frequency of the potential difference induced in one electromagnet coil by the moving permanent magnet; a drive current of matching frequency was passed through the second electromagnet to maintain vibration at the resonant frequency.

Temperature was monitored with 100 Ω RTDs (R1 and R2) in the bottoms of blocks S1 and S2. The experimental temperature was assumed to be the same as that measured by the RTD R2. Temperature was generally maintained to within 0.02 K in both the upper and lower blocks. A third calibrated secondary standard 100 Ω RTD R3 (Rosemont, Inc.), passed through the upper block and was inserted in the top of the lower block. The temperature gradient in the lower block was such that the top of the block was 0.02 K cooler at $T = 323$ K and 0.8 K cooler at $T = 523$ K. Accuracy of the temperature measurements is thought to vary from ± 0.02 K at $T = 323$ K to ± 0.4 K at $T = 523$ K. Random temperature fluctuations of less than 0.01 K over a period of 1 h did not affect τ ; however, rapid changes in temperature of $\geq 3 \cdot 10^{-5}$ K \cdot s $^{-1}$ had a significant effect on τ . R1 and R2 were calibrated against R3 by placing the RTDs in closely spaced holes in block S2 and suspending the block in the tube-furnace.

Fluids were delivered to the densitometer tube with a twin-barrelled positive displacement proportioning pump (Ruska, Inc.). Initial solutions having molalities 5.484 mol \cdot kg $^{-1}$ and 1.008 mol \cdot kg $^{-1}$ of NaCl were prepared from distilled deionized water and reagent-grade NaCl (Mallinckrodt), with molalities determined gravimetrically by desiccation as described by Oakes *et al.*⁽¹⁾ The delivery system for moving initial and diluted solutions to the densitometer is shown schematically in figure 1, and the following discussion refers to this figure.

Tubular Teflon bags (of ≈ 300 cm 3 capacity) filled with Ar-sparged solutions were placed in thermostatted high-pressure reservoirs S. The Teflon bags were sealed at each end by heat shrinkage around Teflon plugs. One of the Teflon plugs in each bag contained a compression fitting through which passed a 1.6 mm o.d. Teflon capillary tube. Each Teflon capillary was attached to a stainless-steel capillary (1.6 mm o.d., 0.8 mm i.d.) which passed through a compression fitting in the cap of the reservoir vessel. Each stainless-steel capillary was connected through a two-way valve V1 and a four-way block B to the densitometer tubing in furnace F. On the effluent side of the densitometer, the capillary was connected to a receiver vessel R which was maintained at the desired experimental pressure with a large-volume Ar ballast A.

Distilled deionized Ar-sparged water was delivered from the pump barrels P1 and P2 through three-way valves V2 and V3 either through the four-way block B and the densitometer or to the reaction vessel S. Water pumped into the reservoir forced solution through V1 and B to the densitometer. Relative proportions of water and

solution passing through the four-way block B could be varied by opening or closing V1 and opening different pairs of ports in valves V2 and V3 and by driving the two pistons P1 and P2 at different rates. Volumetric delivery ratios of 5/1, 2/1, 1/1, 1/2, and 1/5 were selected by changing drive rates. The pump barrels and solution reservoirs were thermostatted between $T = 298 \text{ K}$ and $T = 299 \text{ K}$; molalities of the diluted solutions at each experimental pressure were calculated from the densities and volumetric flow rates of the initial solution and water at the reservoir and pump temperatures and pressures.

Fluids were pumped through the densitometer at volumetric rates between $5.3 \cdot 10^{-3} \text{ cm}^3 \cdot \text{s}^{-1}$ and $5.8 \cdot 10^{-3} \text{ cm}^3 \cdot \text{s}^{-1}$. At these flow rates, the tendency to cool the densitometer assembly was reduced while each successive fluid was purged from the densitometer in a reasonably short time. Measurement of τ was made under constant-flow conditions. Stable values of τ were generally observed within 30 min to 45 min.

Pressure was measured with two transducers (1 MPa to 20.7 MPa and 10 MPa to 103.4 MPa ranges; Precise Sensors, Inc.) each of which was accurate to $\delta p/p_{\text{max}} = 10^{-3}$, where p_{max} is the upper pressure bound of the transducer. Pressure could be monitored in the pump barrels, reservoirs, or in the receiver. The pressure of the receiver was taken as the experimental pressure as there was a minimal pressure drop between it and the densitometer tube. The pressure differential between the pump barrels and the receiver was generally about 0.01 MPa to 0.03 MPa. In spite of the large volume of the Ar ballast A, at $p = 40 \text{ MPa}$ pressure generally increased at a rate of about $8 \text{ Pa} \cdot \text{s}^{-1}$. This regular change in pressure introduced no detectable short-term instability in τ .

The difference in densities $\delta\rho$ of fluids contained in the vibrating tube is related to the vibrational period τ of the densitometer as:

$$\delta\rho = \rho_1 - \rho_2 = \kappa(\tau_1^2 - \tau_2^2), \quad (1)$$

where the proportionality constant κ is dependent on temperature and pressure and may be determined by measuring τ for two fluids of known densities at the appropriate temperature and pressure:

$$\kappa = (\rho_0 - \rho_2)/(\tau_0^2 - \tau_2^2). \quad (2)$$

As the vibrating-tube instrument gives, after calibration, the relative density between a fluid of unknown density and a reference fluid, the ultimate accuracy of the reported V_{ϕ} s is dependent both on the accuracy of the measured τ for the two fluids and on the accuracy of the reference-fluid densities ρ_0 and ρ_2 . Distilled deionized water was used as one density standard at all conditions of this study while $m = 5.484 \text{ mol} \cdot \text{kg}^{-1}$ of NaCl(aq), mass fraction 0.99996 of D₂O, and Ar were used as complementary reference fluids. Densities of water were calculated from the equation of state for water of Haar *et al.*,⁽¹⁴⁾ while densities for 5.484 mol · kg⁻¹ of NaCl(aq) and mass fraction 0.99996 of D₂O were calculated from the equations of Rogers and Pitzer⁽¹¹⁾ and Hill *et al.*,⁽¹⁵⁾ respectively. Densities of Ar at $T = 423 \text{ K}$ and $p = 0.1 \text{ MPa}$ were calculated assuming it to be an ideal gas. Values for κ calculated from these pairs were fit as a cubic function of temperature with reduced weight assigned

to the $T = 523$ K, $m = 5.484$ mol·kg⁻¹ (sodium chloride + water) pair due to possible corrosion or adsorption of salt on the tube and lower confidence in the reported⁽¹¹⁾ density of NaCl(aq) at this temperature. The calibration constant κ for the apparatus used in this study was found to be independent of pressure within experimental uncertainty in the calibration measurements.

3. Results

V_{ϕ} s were calculated from $\delta\rho$ and ρ_0 of Haar *et al.*⁽¹⁴⁾ according to the relation:

$$V_{\phi} = \{-(\rho - \rho_0)/m\rho\rho_0\} + M/\rho, \quad (3)$$

where $M = 58.443$ g·mol⁻¹, m is the molality of NaCl(aq), and ρ and ρ_0 are the densities of the solution and water, respectively. V_{ϕ} s for each experimental temperature, pressure, and NaCl(aq) molality are listed in table 1.

The V_{ϕ} s from this study and the $T = 298$ K and $T = 308$ K results of Oakes *et al.*⁽¹⁾ at $p = 0.1$ MPa have been represented with a temperature- and pressure-dependent form of the Pitzer ion-interaction model. The dependence of V_{ϕ} on m^{-1} was recognized through assignment of reduced weight in the fit at lower molalities.

The volumetric expression of the Pitzer ion-interaction model for a 1-1 strong electrolyte may be written as:

$$V_{\phi} = V_{\phi}^{\infty} + (A_V/b)\ln\{1 + b(m/m^{\circ})^{1/2}\} + 2RT(m/m^{\circ})\{B^V + (m/m^{\circ})C^V\}, \quad (4)$$

where V_{ϕ}^{∞} is the partial molar volume of the neutral salt at infinite dilution; $m^{\circ} = 1$ mol·kg⁻¹; A_V is the volumetric Debye-Hückel limiting-law slope as defined by Bradley and Pitzer⁽¹⁶⁾ and incorporates the equation for the dielectric constant of water by Archer and Wang⁽¹⁷⁾ and the equation of state for water of Hill,⁽¹⁸⁾ B^V and C^V are the second and third virial coefficients; $b = 1.2$; and $R = 8.3144$ J·K⁻¹·mol⁻¹. The second virial coefficient is assumed to vary with ionic strength as:

$$B^V = \beta^{(0)V} + 2\beta^{(1)V}\{1 - (1+x) \cdot \exp(-x)\}/x^2, \quad (5)$$

where $x = \alpha(m/m^{\circ})^{1/2}$ and $\alpha = 2.0$. The V_{ϕ} values determined in this study, as well as those considered by Rogers and Pitzer⁽¹¹⁾ were found to be represented adequately with $\beta^{(1)V} = 0$ at all experimental conditions, although Archer⁽¹³⁾ has included $\beta^{(1)V} \neq 0$ in his treatment of the available results. V_{ϕ}^{∞} and B^V were assumed to vary with temperature and pressure, while C^V was found to be independent of pressure. The latter observation again follows that of Rogers and Pitzer,⁽¹¹⁾ but differs from that of Archer, who included a dependence of C^V on pressure. The pressure- and temperature-dependent expressions used here for these parameters are:

$$V_{\phi}^{\infty}/(\text{cm}^3 \cdot \text{mol}^{-1}) = c_1 + \beta_T p^{\circ} \{c_2 + (c_3/T_x) + c_4 T/T^{\circ}\}, \quad (6)$$

$$B^V = c_5 + c_6(T/T^{\circ})^2 + c_7(T/T^{\circ}) + c_8/T_x + (p/p^{\circ})\{c_9(T/T^{\circ})^2 + c_{10} T/T^{\circ}\}, \quad (7)$$

$$C^V = c_{11} + c_{12}(T/T^{\circ})^2 + c_{13}(T/T^{\circ}) + c_{14}/T_x, \quad (8)$$

TABLE 1. Apparent molar volumes V_{ϕ} of NaCl(aq) calculated from measured relative densities, and differences δV_{ϕ} as calculated from equation (4)

m mol · kg ⁻¹	V_{ϕ} cm ³ · mol ⁻¹	δV_{ϕ} cm ³ · mol ⁻¹	m mol · kg ⁻¹	V_{ϕ} cm ³ · mol ⁻¹	δV_{ϕ} cm ³ · mol ⁻¹	m mol · kg ⁻¹	V_{ϕ} cm ³ · mol ⁻¹	δV_{ϕ} cm ³ · mol ⁻¹
$T = 298.09 \text{ K, } p = 7.30 \text{ MPa}$								
5.484	21.33	0.00	0.837	18.41	-0.12	1.696	19.35	0.05
4.483	20.94	0.01	0.499	18.10	-0.05	0.833	18.58	0.05
3.519	20.94	0.03	0.166	17.85	0.23	1.008	18.52	-0.18
2.591	19.97	0.04	5.484	21.33	0.00	0.668	18.16	-0.19
1.696	19.43	0.13	4.483	20.93	0.00	0.332	17.83	-0.08
0.833	18.76	0.23	3.519	20.49	0.02			
1.008	18.48	-0.22	2.591	19.96	0.03			
$T = 298.05 \text{ K, } p = 41.5 \text{ MPa}$								
5.484	22.05	-0.07	0.668	19.49	0.10	0.830	20.05	0.50
3.513	21.40	0.05	0.332	19.42	0.44	0.837	19.57	0.01
1.690	20.50	0.23	4.479	21.74	-0.07	0.499	19.42	0.22
1.008	19.73	0.01	2.584	21.40	0.05	0.165	19.35	0.65
$T = 323.18 \text{ K, } p = 7.05 \text{ MPa}$								
5.484	22.04	-0.04	0.668	19.61	-0.14	1.696	20.40	-0.05
4.483	21.70	0.00	0.332	19.10	-0.28	1.008	19.87	-0.15
2.591	20.87	-0.03	5.484	22.03	-0.05	0.499	19.36	-0.22
0.833	19.88	-0.01	3.519	21.33	0.03	0.165	18.91	-0.19
$T = 323.19 \text{ K, } p = 40.5 \text{ MPa}$								
5.484	22.61	-0.08	0.499	20.43	-0.06	0.830	20.72	-0.04
3.513	22.03	0.02	0.165	19.68	-0.37	0.667	20.43	-0.21
1.690	21.29	0.03	4.479	22.34	-0.01	0.331	20.12	-0.19
1.008	20.65	-0.23	2.584	21.70	0.05			
$T = 372.71 \text{ K, } p = 7.15 \text{ MPa}$								
5.484	21.93	0.01	0.499	18.58	-0.25	0.833	19.21	-0.06
3.519	21.07	0.05	0.165	17.93	-0.17	0.668	18.93	-0.14
1.696	19.97	-0.03	4.483	21.52	0.05	0.332	18.24	-0.29
1.008	19.29	-0.16	2.591	20.58	0.04			
$T = 373.00 \text{ K, } p = 40.9 \text{ MPa}$								
5.484	22.60	0.02	0.331	19.67	-0.01	0.499	19.91	-0.03
3.513	21.91	0.11	4.479	22.26	0.07			
1.690	21.11	0.17	2.584	21.54	0.14			
0.667	20.11	-0.03	1.008	20.46	-0.01			
$T = 373.00 \text{ K, } p = 40.1 \text{ MPa}$								
5.484	22.61	0.03	1.691	21.04	0.10	2.584	21.50	0.10
3.513	21.81	0.01	4.479	22.19	0.00	0.830	20.10	-0.21
$T = 423.00 \text{ K, } p = 7.30 \text{ MPa}$								
1.008	16.08	-0.14	0.165	13.87	0.14	0.332	14.58	0.06
0.837	15.91	0.02	1.008	15.99	-0.23			
0.499	15.05	-0.03	0.668	15.53	0.01			
$T = 423.00 \text{ K, } p = 7.15 \text{ MPa}$								
5.484	20.28	0.01	1.696	17.23	0.01	2.591	18.15	-0.02
4.483	19.67	0.03	5.484	20.25	-0.02	0.833	16.04	0.16
2.591	18.22	0.05	3.519	18.95	0.00			

TABLE 1—continued

m mol·kg ⁻¹	V_ϕ cm ³ ·mol ⁻¹	δV_ϕ cm ³ ·mol ⁻¹	m mol·kg ⁻¹	V_ϕ cm ³ ·mol ⁻¹	δV_ϕ cm ³ ·mol ⁻¹	m mol·kg ⁻¹	V_ϕ cm ³ ·mol ⁻¹	δV_ϕ cm ³ ·mol ⁻¹
$T = 423.00 \text{ K}, p = 41.4 \text{ MPa}$								
5.484	21.35	-0.03	0.331	17.22	0.67	0.499	17.23	0.22
0.667	17.64	0.26	1.008	17.94	-0.02			
$T = 423.00 \text{ K}, p = 40.2 \text{ MPa}$								
5.484	21.26	-0.12	1.691	18.63	-0.16	2.584	19.47	-0.12
3.513	20.16	-0.09	4.479	20.75	-0.09	0.830	17.78	0.10
$T = 472.94 \text{ K}, p = 7.20 \text{ MPa}$								
5.484	16.69	0.09	0.668	8.17	0.11	0.833	8.53	-0.22
3.519	14.34	-0.02	0.332	6.69	0.55	0.837	9.19	0.43
1.696	11.15	-0.11	4.483	15.57	0.03	0.499	7.47	0.26
1.008	9.29	-0.09	2.591	12.88	-0.10			
$T = 475.96 \text{ K}, p = 7.10 \text{ MPa}$								
5.484	16.39	0.11	1.696	10.71	-0.01	2.591	12.46	-0.06
3.519	14.03	0.08	4.483	15.33	0.15	0.833	8.38	0.27
$T = 472.95 \text{ K}, p = 41.2 \text{ MPa}$								
5.484	18.68	-0.04	0.499	11.66	0.36	0.830	12.80	0.32
3.513	16.88	-0.01	0.165	10.09	0.79	0.667	12.17	0.22
1.690	14.43	0.00	4.479	17.75	-0.10	0.331	11.19	0.71
1.008	12.95	-0.02	2.584	15.75	-0.04			
$T = 475.96 \text{ K}, p = 40.1 \text{ MPa}$								
5.484	18.39	-0.05	1.691	14.02	0.04	2.584	15.25	-0.14
3.513	16.60	0.06	4.479	17.54	0.01	0.830	12.20	0.25
$T = 522.97 \text{ K}, p = 7.10 \text{ MPa}$								
5.484	9.55	-0.13	1.008	-5.66	-0.07	2.591	2.12	-0.01
4.483	7.47	0.01	0.499	-10.43	-0.08	1.696	-1.67	-0.14
3.519	5.06	0.06	0.165	-15.68	0.54	0.833	-6.61	0.35
2.591	2.14	0.02	5.484	9.54	-0.14	0.668	-8.68	-0.20
1.696	-1.54	-0.01	4.483	7.48	0.02	0.332	-12.31	0.44
0.833	-6.81	0.15	3.519	5.05	0.05			
$T = 522.98 \text{ K}, p = 40.9 \text{ MPa}$								
5.484	13.92	0.02	0.830	3.24	0.53	3.513	10.78	0.16
4.479	12.44	0.12	0.667	1.08	-0.66	2.584	8.61	-0.07
3.513	10.79	0.17	0.331	-1.37	-0.34	1.690	6.15	-0.11
2.584	8.79	0.11	5.484	13.96	0.06	1.008	3.34	-0.28
1.690	6.29	0.03	4.479	12.43	0.10	0.499	0.15	-0.37
$T = 520.37 \text{ K}, p = 40.2 \text{ MPa}$								
5.484	14.02	-0.13	0.830	3.03	-0.23	1.691	6.46	-0.25
3.513	10.91	-0.05	4.479	12.64	0.02			
2.584	8.93	-0.14	3.513	11.01	0.05			

where $T_x = (T/T^\circ) - 227$, $T^\circ = 1 \text{ K}$, $p^\circ = 1 \text{ MPa}$, and $\beta_T = (\partial \ln \rho / \partial p)_T$ is the isothermal compressibility coefficient of water. Values of the parameters c_1 to c_{14} are listed in table 2. Figure 2 shows each of the molality-independent quantities as a function of temperature. β_T was chosen as an independent variable to represent the

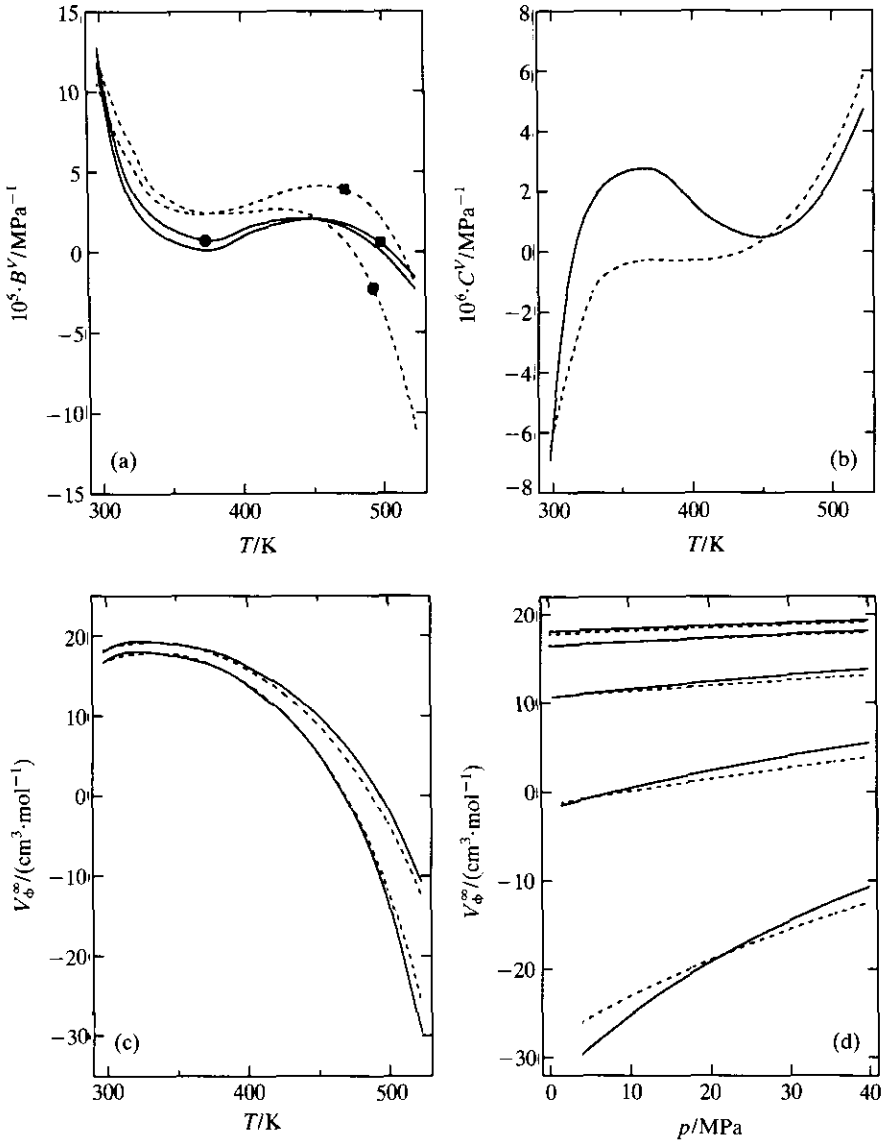


FIGURE 2. The parameters (a), B^V , (b), C^V , and (c), V_{ϕ}^{∞} plotted against T at: \bullet , $p = p_{\text{sat}}$ (0.1 MPa for $T \leq 373.15$ K); and \blacksquare , $p = 40$ MPa. (d), V_{ϕ}^{∞} plotted against p ; —, this work; ---, Rogers and Pitzer.⁽¹¹⁾

pressure dependence of V_{ϕ}^{∞} because a simpler functional form was obtained as compared with fits in which pressure was taken to be the independent variable. The simple linear dependence of $\beta^{(0)V}$ on pressure given in equation (7) was sufficient to represent the experimental results presented here, while C^V as given by equation (8) was taken to be independent of pressure. Thus all non-linearity of the pressure dependence of V_{ϕ} in the present representation is contained in the infinite-dilution

TABLE 2. Coefficients for equations (6) through (8) describing the temperature and pressure dependence of the parameters V_ϕ^∞ , B^V , and C^V

Coefficient	Estimate	Coefficient	Estimate	Coefficient	Estimate
c_1	30.897	c_6	$-1.0560 \cdot 10^{-8}$	c_{11}	$2.8903 \cdot 10^{-4}$
c_2	$2.1987 \cdot 10^4$	c_7	$1.0450 \cdot 10^{-5}$	c_{12}	$1.0987 \cdot 10^{-9}$
c_3	$-1.4279 \cdot 10^6$	c_8	$5.1618 \cdot 10^{-2}$	c_{13}	$-1.0862 \cdot 10^{-6}$
c_4	$-1.1195 \cdot 10^3$	c_9	$5.2865 \cdot 10^{-12}$	c_{14}	$-4.9639 \cdot 10^{-3}$
c_5	$-2.7750 \cdot 10^{-3}$	c_{10}	$-2.3790 \cdot 10^{-9}$		

intercept V_ϕ^∞ . Majer *et al.*⁽⁹⁾ found that their measurements at high temperatures could not be represented quantitatively by assuming a linear pressure dependence of V_ϕ , and both Rogers and Pitzer⁽¹¹⁾ and Archer⁽¹³⁾ included quadratic pressure terms in their overall representations for V_ϕ .

Smoothed values of V_ϕ calculated from equation (4) at round molalities at the solvent vapor-saturation pressure and at $p = 40$ MPa are presented in table 3.

4. Discussion

The model and its molality-independent parameters used to represent the results in this study are the same as those used by Rogers and Pitzer⁽¹¹⁾ and therefore the

TABLE 3. V_ϕ for NaCl(aq) at $p = p_{\text{sat}}$ and $p = 40$ MPa

$m/(\text{mol} \cdot \text{kg}^{-1})$:	0	0.10	0.25	0.50	1.00	2.00	4.00	5.50
T/K								
					$p = p_{\text{sat}}^a$			
298.15	16.66	17.22	17.53	17.91	18.46	19.30	20.51	21.15
323.15	18.06	18.71	19.03	19.37	19.81	20.43	21.35	21.95
348.15	17.76	18.60	18.99	19.38	19.87	20.50	21.42	22.06
373.15	16.40	17.51	18.03	18.54	19.17	19.97	21.06	21.77
398.15	14.09	15.58	16.28	16.97	17.82	18.89	20.27	21.11
423.15	10.65	12.69	13.65	14.59	15.76	17.20	19.01	20.03
448.15	5.70	8.54	9.87	11.18	12.79	14.74	17.13	18.43
473.15	-1.51	2.54	4.42	6.26	8.51	11.21	14.45	16.19
498.15	-12.40	-6.42	-3.66	-0.97	2.29	6.15	10.71	13.14
523.15	-29.67	-20.39	-16.13	-11.99	-7.03	-1.21	5.59	9.21
T/K								
					$p = 40$ MPa			
298.15	18.00	18.52	18.82	19.17	19.68	20.45	21.55	22.10
323.15	19.31	19.90	20.18	20.48	20.87	21.40	22.18	22.69
348.15	19.15	19.88	20.22	20.55	20.96	21.49	22.25	22.79
373.15	18.12	19.06	19.49	19.92	20.44	21.10	22.00	22.59
398.15	16.35	17.58	18.16	18.73	19.43	20.30	21.44	22.14
423.15	13.80	15.43	16.20	16.95	17.89	19.06	20.53	21.38
448.15	10.29	12.47	13.49	14.50	15.75	17.28	19.20	20.26
473.15	5.49	8.44	9.81	11.17	12.83	14.85	17.33	18.69
498.15	-1.19	2.88	4.77	6.61	8.85	11.53	14.78	16.59
523.15	-10.71	-4.94	-2.29	0.27	3.37	7.02	11.41	13.86

^a $p = 0.1$ MPa at $T \leq 373.15$ K.

parameter values should be comparable. As noted above, Archer⁽¹³⁾ included a dependence on pressure of $\beta^{(1)}$, leading to $\beta^{(1)V} \neq 0$, and his representation is less directly comparable to the present treatment due to the correlation of $\beta^{(0)}$ and $\beta^{(1)}$ in the calculation of the second virial coefficient B . The parameters B^V and C^V determined from the values measured in this study are compared with those determined by Rogers and Pitzer⁽¹¹⁾ in figure 2. The general trends of each of them are very similar, although Rogers and Pitzer's⁽¹¹⁾ B^V term, which includes a quadratic dependence on pressure, has a larger pressure dependence than the corresponding quantity determined in this work, particularly at $T > 373$ K. Also, B^V calculated from equation (7) shows a slightly more complex dependence on temperature. The dependence of B^V on temperature is not as large as that of Rogers and Pitzer⁽¹¹⁾ at the high-temperature bound of the present study, and the dependence of C^V is larger than Rogers and Pitzer's at low temperatures. These differences are offset by the partial cancellation of the contributions of the respective terms to V_{ϕ} .

Although small differences are expected due to the treatment of different sets of experimental results and the use of different functions to extrapolate V_{ϕ} to infinite dilution, values of V_{ϕ}^{∞} obtained in this work should be comparable with those determined in other studies. V_{ϕ}^{∞} s reported to $T = 473.15$ K at $p = 2$ MPa by Ellis⁽²⁾ are in good agreement with those of this study at $T \leq 373.15$ K, but differ by about $2 \text{ cm}^3 \cdot \text{mol}^{-1}$ at $T = 423.15$ and $T = 473.15$ K. This disagreement may be due in part to Ellis's⁽²⁾ method for extrapolating to infinite dilution, which did not include the Debye-Hückel limiting law.

Majer *et al.*⁽⁹⁾ tabulated V_{ϕ}^{∞} s determined from their measurements to $T = 373.15$ K at $p = 0.1$ MPa, and to $T = 598.15$ K at $p = 20$ MPa and $p = 40$ MPa. Differences δV_{ϕ}^{∞} between their V_{ϕ}^{∞} s and those of this study are smaller than $0.4 \text{ cm}^3 \cdot \text{mol}^{-1}$ at all pressures for $T \leq 423.15$ K. At $p = 20$ MPa, $|\delta V_{\phi}^{\infty}| \leq 1 \text{ cm}^3 \cdot \text{mol}^{-1}$ for all $T \leq 523.15$ K. However, V_{ϕ}^{∞} s at $p = 40$ MPa calculated from equation (6) are significantly less negative than those of Majer *et al.*⁽⁹⁾ at $T = 473.15$ K and $T = 523.15$ K, with differences as large as $3.1 \text{ cm}^3 \cdot \text{mol}^{-1}$ at $T = 523.15$ K. The disagreement with Majer *et al.* may be due in part to their extrapolation to $p = 40$ MPa assuming a linear dependence of V_{ϕ} on pressure.

Comparisons of the values of V_{ϕ}^{∞} calculated from equation (6) with those taken from Rogers and Pitzer⁽¹¹⁾ and Archer⁽¹³⁾ are given in table 4. Agreement of the values is generally very good, with the largest $|\delta V_{\phi}^{\infty}| = 3.71 \text{ cm}^3 \cdot \text{mol}^{-1}$ between our V_{ϕ}^{∞} and that of Rogers and Pitzer⁽¹¹⁾ at $T = 523.15$ K and $p = p_{\text{sat}}$. This relatively large difference is probably a result of Rogers and Pitzer's dependence on Hilbert's⁽⁴⁾ measurements at $T > 473$ K. Hilbert's measurements at $T > 523$ K were made at $p \geq 20$ MPa, and therefore Rogers and Pitzer's estimates of V_{ϕ}^{∞} at saturation pressure represent rather long extrapolations in pressure at this temperature. At $T \geq 348.15$ K our V_{ϕ}^{∞} s are systematically lower than those calculated by Archer,⁽¹³⁾ although the values are always within $2 \text{ cm}^3 \cdot \text{mol}^{-1}$. As noted above, Archer,⁽¹³⁾ included $\beta^{(1)V} \neq 0$ in his fit of a comprehensive set of experimental results. The contribution of the term in $\beta^{(1)V}$ to V_{ϕ} introduces a non-linear dependence of the second virial coefficient of the Pitzer equations which is most significant at low

TABLE 4. Apparent molar volumes of NaCl(aq) at infinite dilution V_{ϕ}^{∞} calculated from equation (6) and deviations δV_{ϕ}^{∞} of literature values

p :	p_{sat}	20 MPa	40 MPa	p_{sat}	20 MPa	40 MPa	p_{sat}	20 MPa	40 MPa
T/K	$V_{\phi}^{\infty}/(\text{cm}^3 \cdot \text{mol}^{-1})$			$\delta V_{\phi}^{\infty}/(\text{cm}^3 \cdot \text{mol}^{-1})^a$			$\delta V_{\phi}^{\infty}/(\text{cm}^3 \cdot \text{mol}^{-1})^b$		
298.15	16.66	17.36	18.00	-0.02	-0.13	-0.23	0.04	-0.19	-0.39
323.15	18.06	18.72	19.31	0.32	0.26	0.21	0.13	0.00	-0.13
348.15	17.76	18.50	19.15	0.06	0.13	0.17	-0.15	-0.24	-0.35
373.15	16.40	17.32	18.12	-0.09	0.09	0.20	-0.45	-0.55	-0.66
398.15	14.09	15.31	16.35	-0.11	0.20	0.37	-0.70	-0.82	-0.96
423.15	10.65	12.37	13.80	-0.05	0.45	0.70	-0.88	-1.03	-1.21
448.15	5.70	8.23	10.29	-0.03	0.76	1.15	-1.00	-1.17	-1.41
473.15	-1.51	2.35	5.49	-0.29	0.95	1.63	-1.05	-1.28	-1.54
498.15	-12.40	-6.18	-1.19	-1.28	0.78	1.92	-1.24	-1.37	-1.63
523.15	-29.67	-19.15	-10.71	-3.71	-0.23	1.76	-1.44	-1.49	-1.67

^a $\delta V_{\phi}^{\infty} = V_{\phi}^{\infty}\{\text{equation (6)}\} - V_{\phi}^{\infty}\{\text{reference 11}\}$.

^b $\delta V_{\phi}^{\infty} = V_{\phi}^{\infty}\{\text{equation (6)}\} - V_{\phi}^{\infty}\{\text{reference 13}\}$.

molalities. The systematic trend in δV_{ϕ}^{∞} calculated from equation (6) and reference 13 points out the need for precise measurements of V_{ϕ} at low molalities in order to determine V_{ϕ}^{∞} with a precision better than that reflected in table 4.

The differences δV_{ϕ} between our model V_{ϕ} values and those from the compilations of Rogers and Pitzer⁽¹¹⁾ and Archer⁽¹³⁾ are plotted in figure 3 against $m^{1/2}$ at various temperatures at $p = p_{\text{sat}}$ and $p = 40$ MPa. Our calculated V_{ϕ} s are in very good agreement with those of Archer⁽¹³⁾ for $m \geq 1 \text{ mol} \cdot \text{kg}^{-1}$, with relatively small systematically negative values of δV_{ϕ} at lower molalities. Comparison with the earlier treatment of Rogers and Pitzer⁽¹¹⁾ shows slightly poorer agreement of V_{ϕ} s at all except the highest molalities. More detailed comparisons of the results of this study with reported densities of NaCl(aq) are given below.

The standard error in the overall fit of equation (4) to the values of V_{ϕ} determined in this study, $0.079 \text{ cm}^3 \cdot \text{mol}^{-1}$, corresponds to a fractional error $\delta\rho/\rho < 4 \cdot 10^{-4}$ in the solution density for the entire range of pressure and temperature of this study. Uncertainties in V_{ϕ} s, estimated from propagation of the uncertainties in τ determined for water and NaCl(aq), are nearly independent of temperature, ranging from $|\delta V_{\phi}| \approx 0.05 \text{ cm}^3 \cdot \text{mol}^{-1}$ at high molalities to $|\delta V_{\phi}| \approx 0.5 \text{ cm}^3 \cdot \text{mol}^{-1}$ at the lowest molalities. However, measurements at $T = 523 \text{ K}$ have larger uncertainties arising from temperature instability as described below, and interlaboratory agreement at $T \geq 473 \text{ K}$ is poor. Hence lower precision in relative density is assumed at the highest temperatures considered here.

For $T \leq 373 \text{ K}$, nearly all of the previously published results agree with the present values within $\delta\rho/\rho \leq 4 \cdot 10^{-4}$. The exceptions are a few values from Hilbert.⁽⁴⁾ As Hilbert's densities are estimated to have $\delta\rho/\rho \leq 10^{-3}$ at $T < 473 \text{ K}$,^(9, 11) the disagreement of the compared measurements is insignificant.

From $T = 398 \text{ K}$ through $T = 448 \text{ K}$, most of the densities reported elsewhere for $m < 3 \text{ mol} \cdot \text{kg}^{-1}$ lie either within or just outside the $\delta\rho/\rho \leq 4 \cdot 10^{-4}$ uncertainty estimated for our measurements. However, the studies of Rogers *et al.*⁽⁷⁾ and Majer

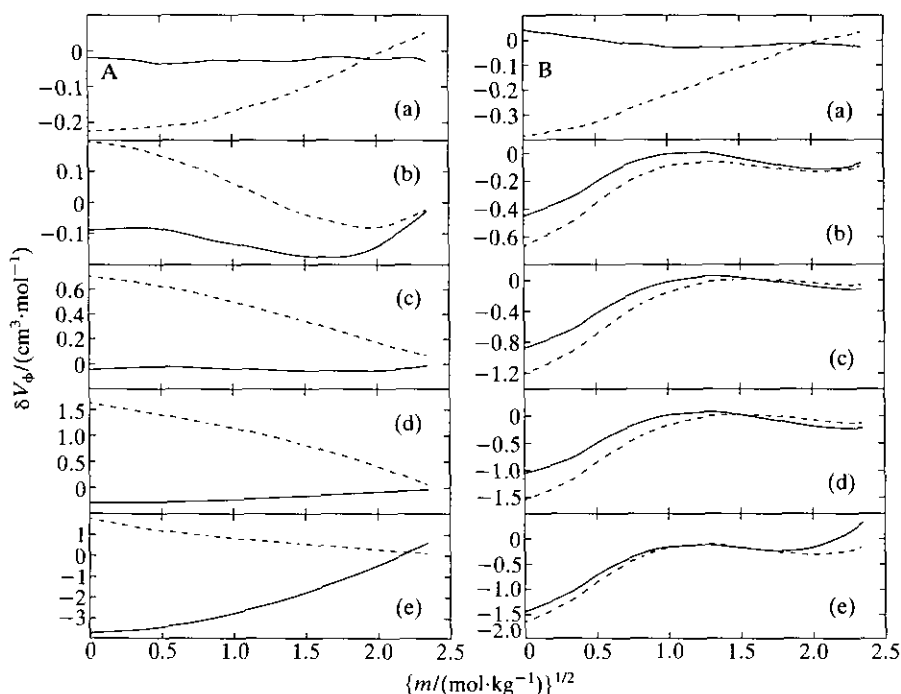


FIGURE 3. $\delta V_{\phi} = V_{\phi}\{\text{equation(4)} - V_{\phi}(\text{A, reference 11 and B, reference 13})\}$ plotted against $m^{1/2}$. —, $p = p_{\text{atm}}$; ---, $p = 40 \text{ MPa}$. (a), $T = 298.15 \text{ K}$; (b), $T = 373.15 \text{ K}$; (c), $T = 423.15 \text{ K}$; (d), $T = 473.15 \text{ K}$; (e), $T = 523.15 \text{ K}$.

et al.⁽⁹⁾ show consistently negative deviations from this study for most of the molality range. At $T = 448 \text{ K}$ and $m > 3 \text{ mol} \cdot \text{kg}^{-1}$, the differences between our measurements and Majer *et al.*'s values are as large as $\delta\rho/\rho = 10^{-3}$.

At $T = 473 \text{ K}$ the differences in solution density reported by other investigators relative to the values obtained in this work increase sharply to $\delta\rho/\rho \approx 10^{-3}$. Grant-Taylor's⁽⁵⁾ density values are generally higher than those determined in this work, with $\delta\rho/\rho$ ranging from $5 \cdot 10^{-4}$ to 10^{-3} . Hilbert's measurements are randomly distributed around our measurements, with $-10^{-3} \leq \delta\rho/\rho \leq 10^{-3}$ over the entire molality range. Rogers *et al.*⁽⁷⁾ and Majer *et al.*⁽⁹⁾ estimate the precision of their measurements as $|\delta\rho/\rho| \leq 5 \cdot 10^{-4}$. At $p \leq 20 \text{ MPa}$ the differences between densities of these studies and the results reported are within $|\delta\rho/\rho| \leq 5 \cdot 10^{-4}$. Within this range, however, densities from these two studies are consistently lower than those reported here, resulting in higher V_{ϕ} s and negative δV_{ϕ} s. The smoothed densities reported at $p = 40 \text{ MPa}$ by Majer *et al.*⁽⁹⁾ are lower than our measurements by as much as $\delta\rho/\rho \approx 10^{-3}$. Part of this discrepancy may result from the use by Majer *et al.*⁽⁹⁾ of an assumed linear pressure dependence in V_{ϕ} to extrapolate from their experimental conditions to $p = 40 \text{ MPa}$.

At $T = 498 \text{ K}$ all of the previously reported measurements other than Grant-Taylor's⁽⁵⁾ values at $m = 2 \text{ mol} \cdot \text{kg}^{-1}$ have $\delta\rho/\rho \leq 10^{-3}$ as compared with our

measurements. The good agreement of the measurements reported by Majer *et al.*⁽⁹⁾ with those of the present study at all experimental pressures supports the hypothesis that their linear extrapolations of V_{ϕ}^{∞} s to $p = 40$ MPa may be unreliable.

At $T = 523$ K, the internal precision of the densities reported here decreases to $|\delta\rho/\rho| \leq 1.8 \cdot 10^{-3}$ ($|\delta\rho/\rho| \approx 8 \cdot 10^{-4}$ from temperature uncertainty and $|\delta\rho/\rho| \approx 10^{-3}$ from uncertainty in κ). Although the densities of Hilbert,⁽⁴⁾ L'vov,⁽⁶⁾ and Grant-Taylor⁽⁵⁾ are generally higher than those reported here, their results are within $\delta\rho/\rho \leq 2 \cdot 10^{-3}$ compared with the results of this study. V_{ϕ}^{∞} s at $p = 20$ MPa calculated from their measurements by Majer *et al.*⁽⁹⁾ are in excellent agreement with those of this study, while their values at $p = 40$ MPa are consistently higher. These authors state that their more recent results⁽¹⁰⁾ at high pressures are consistent with their first results,⁽⁹⁾ while their new measurements at low pressures are substantially larger. Our recent densities at $T = 523$ K and $p = 7$ MPa using a new (platinum + iridium) vibrating-tube densitometer (with water and helium as reference fluids) are somewhat higher than the values reported here ($\delta\rho/\rho \approx 1.4 \cdot 10^{-3}$ at $m = 6 \text{ mol} \cdot \text{kg}^{-1}$). However, our new results at $p = 40$ MPa are virtually identical to those presented in this report ($\delta\rho/\rho \approx 10^{-4}$ at $m = 6 \text{ mol} \cdot \text{kg}^{-1}$). Completion of density measurements with our new vibrating-tube densitometer and a complete treatment of all available volumetric values at high temperatures are needed to resolve the apparent disagreement in measured densities at high pressures for $T = 523$ K.

The densities obtained in this study are in generally good agreement with the literature values in the pressure and temperature region at and below 523 K and 40 MPa. The pressure and temperature form of the Pitzer ion-interaction model used to represent V_{ϕ} appears to behave well at conditions well removed from our experimental conditions. This model is of simpler form than those presented by Rogers and Pitzer⁽¹¹⁾ and Archer.⁽¹³⁾ However, these earlier critical compilations include a wider range of experimental results and span wider ranges of temperature and pressure than were considered in developing the model equations reported here; one of these more complete treatments should be used in preference to the present work for general calculations of volumetric properties of NaCl(aq). A non-linear pressure dependence in V_{ϕ}^{∞} is necessary to reproduce the experimental results accurately, and was incorporated through an assumed linear dependence of V_{ϕ}^{∞} on β_T . As a result of this choice of independent variable, the non-linearity of V_{ϕ}^{∞} with pressure increases with increasing temperature.

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