Volumetric Properties of Aqueous Sodium Hydroxide from 273.15 to 348.15 K

John M. Simonson* and Robert J. Ryther[†]

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

Densities of aqueous sodium hydroxide solutions were measured with a vibrating tube densimeter from 0.06 to 25.2 mol·kg⁻¹ at temperatures from 278 to 318 K and pressures from 0.7 to 34.4 MPa. Values of the apparent molar volumes V_ϕ calculated from the measured densities are compared with available literature results at similar experimental conditions. The V_ϕ are correlated as functions of temperature, pressure, and composition with the volumetric form of the ion interaction model to moderately high molalities; an arbitrary power series in $m^{1/2}$ is used at higher molalities. Specific volumes of NaOH(aq) are tabulated at smoothed temperatures, pressures, and molalities. Standard-state partial molar volumes, expansivities, compressibilities, and heat capacities calculated from the treatment are consistent with the reaction thermodynamic properties of water and available values for NaCl(aq) and HCl(aq).

Introduction

The volumetric properties of aqueous base solutions are of interest in a number of industrial and geochemical applications. A knowledge of the density and compressibility of NaOH(aq) is required to analyze the results of other thermodynamic measurements, including flow calorimetric experiments. The high solubility of sodium hydroxide in water presents a severe test of the range of applicability of semiempirical representations of solution densities. In the present work a vibrating tube densimeter was used to determine densities of NaOH(aq) to 25 mol·kg⁻¹ at temperatures from 278 to 318 K and pressures from 0.7 to 35 MPa. These results are compared with other available density measurements. A consistent set of the available results is treated with the ion interaction model through the upper molality limit of applicability. An arbitrary power series in $m^{1/2}$ is fitted to the results at higher molalities. Smooth values of volumetric properties calculated at regular intervals in temperature, pressure, and composition are tabulated. As a check of the consistency of the treatment, the reaction thermodynamic properties for the ionization of water are calculated with the standard-state partial molar quantities for NaOH(aq) obtained in this work.

Experimental Section

Eleven solutions were prepared by weight dilution of 50% analytical grade NaOH(aq) (Fisher Scientific). Final molalities of the diluted solutions ranged from 0.06 to 25.2 mol·kg⁻¹. Solutions were handled in argon atmosphere and stored under argon in high density polyethylene bottles to avoid contamination by atmospheric CO_2. Addition of barium hydroxide to a 1 mol·kg⁻¹ solution gave no indication of carbonate contamination. All base solutions were standardized to better than ±0.1% by titration with standard hydrochloric acid.

Relative densities were measured with a vibrating tube densimeter with a stainless steel u-tube (Mettler-Paar Model 512). Measurements of the period of vibration were within ±1 ppm. The cell was thermostated with a refrigerated circulating bath.

[†] ORNL-GLCA/ACM Research Student, Earlham College, Earlham, IN.

The bath temperature and the temperature of the vibrating tube mounting block were measured to ±0.01 K with calibrated platinum resistance thermometers. Pressures were generated with a hand-operated pump (HIP Equipment Co.) and measured to ±0.01-MPa precision with a compensated Bourdon tube pressure gauge (Ashcroft Digigage).

Calibrations of the densimeter were performed frequently with deionized distilled water and 5.000 mol·kg⁻¹ NaCl(aq) reference fluids. Densities of water at experimental conditions were calculated from the equation of state of Haar, Gallagher, and Kell (1); densities of the reference NaCl(aq) were calculated from the low-temperature ion interaction representation given by Rogers and Pitzer (2). The accuracy of these reference density values is taken to be within 100 ppm over the temperature and pressure ranges of interest here.

At a given temperature, the vibrating tube was filled with water and the period measured at three pressures (0.7, 20.7, and 34.4 MPa). This calibration series was repeated with standard NaCl(aq), followed by measurements on the NaOH(aq) solutions. Repeat calibrations were carried out at regular intervals (about 4 h between calibrations) to ensure against drift or shifting of the oscillator frequency over time. Replicate measurements indicated experimental precision within 100 ppm in the relative density.

Results and Model Equations

The measured frequencies of the vibrating tube give the relative densities of NaOH(aq). These values were used with the equation of state for water of ref 1 to calculate the apparent molar volume V_ϕ through

$$V_\phi = -1000(\rho - \rho_0)/m\rho\rho_0 + M_2/\rho \qquad (1)$$

where ρ is the solution density, ρ_0 is the density of water, M_2 is the formula weight of the solute, and m is the molality. Values of V_ϕ are listed in Table I.

The ion interaction treatment of electrolyte solution thermodynamics developed by Pitzer (3) has been applied to a wide variety of experimental results over broad ranges of temperature, pressure, and solution composition. Of particular interest in this work is the pressure derivative form of the model, giving a parametric equation for the apparent molar volume. The equations have been used by Rogers and Pitzer (2) in their correlation of the available volume data for NaCl(aq). Pabalan and Pitzer (4) recently applied this treatment to the apparent molar volume data for NaOH(aq) to 623 K at saturation pressure. A more limited temperature range is considered here, and the results in high and low molality ranges are treated separately in order to obtain a more accurate representation of the available results at low molalities near ambient temperature. Apparent molar compressibilities κ_ϕ calculated from the V_ϕ values at high pressures are fitted consistently with literature values determined from sound-speed measurements.

The ion interaction expression for the apparent molar volume is

$$V_\phi = \bar{V}^\circ_2 + \nu|z_M z_X|A_V h(I) + 2\nu_M\nu_X RT[mB^V + m^2(\nu_M z_M)C^V] \qquad (2)$$

where ν, ν_M, and ν_X are the number of ions, cations, and anions,

Table I. Measured Apparent Molar Volumes of NaOH(aq)

$m/$ (mol·kg⁻¹)	277.73 K	287.74 K	297.26 K	307.74 K	317.48 K
	V_ϕ at 0.69 MPa				
0.0601	−8.539	−6.591	−5.091	−5.597	−5.047
0.1005	−7.536	−6.131	−4.850	−4.557	−4.053
0.2025	−7.491	−5.557	−4.290	−3.956	−3.268
0.4937	−6.413	−4.721	−3.568	−2.939	−2.325
1.0202	−5.068	−3.470	−2.540	−1.869	−1.378
2.0303	−2.748	−1.630	−0.678	−0.179	0.183
4.0570	0.372	1.115	1.714	2.090	2.350
6.0890	2.618	3.198	3.545	3.924	4.101
10.1434	5.843	6.258	6.508	6.696	6.858
15.2540	8.638	8.949	9.142	9.290	9.427
25.0202	11.768	12.028	12.151	12.261	12.381
	V_ϕ at 20.68 MPa				
0.0601	−6.353	−4.713	−4.532	−3.443	−3.631
0.1005	−5.284	−4.278	−3.735	−2.783	−2.669
0.2025	−5.445	−3.860	−3.110	−2.322	−2.009
0.4937	−4.589	−3.150	−2.246	−1.611	−1.102
1.0202	−3.455	−2.091	−1.315	−0.659	−0.266
2.0303	−1.348	−0.410	0.382	0.878	1.163
4.0570	1.461	2.084	2.588	2.943	3.152
6.0890	3.502	3.992	4.279	4.637	4.771
10.1434	6.467	6.823	7.037	7.201	7.351
15.2540	9.075	9.347	9.515	9.649	9.779
25.0202	12.030	12.264	12.375	12.478	12.595
	V_ϕ at 34.47 MPa				
0.0601	−4.282		−2.357	−6.592	−3.210
0.1005	−3.648		−2.387	−4.239	−1.976
0.2025	−3.934	−2.360	−1.908	−2.592	−1.273
0.4937	−3.358	−2.014	−1.279	−1.215	−0.372
1.0202	−2.362	−1.116	−0.471	−0.091	0.424
2.0303	−0.440	0.388	1.097	1.459	1.784
4.0570	2.163	2.702	3.165	3.459	3.663
6.0890	4.070	4.489	4.753	5.074	5.200
10.1434	6.867	7.180	7.378	7.518	7.665
15.2540	9.353	9.594	9.755	9.869	10.003
25.0202	12.196	12.409	12.518	12.608	12.730

respectively, z_M and z_X are the ionic charges, and A_V is the limiting slope for the apparent molar volume as defined by Bradley and Pitzer (5). The partial molar volume at infinite dilution is $\bar{V}°_2$, $R = 8.31441$ cm³·MPa·K⁻¹·mol⁻¹, and T is the absolute temperature. The limiting law function is given by

$$h(I) = \ln(1 + bI^{1/2})/2b \qquad (3)$$

with $b = 1.2$ kg$^{1/2}$·mol$^{-1/2}$. The volumetric second virial coefficient is a function of ionic strength given by

$$B^V = \beta^{(0)V} + 2\beta^{(1)V}[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})]/\alpha^2 I \qquad (4)$$

The coefficient $\alpha = 2.0$ kg$^{1/2}$·mol$^{-1/2}$, and the interaction parameters are

$$\beta^{(0)V} = (\partial\beta^{(0)}/\partial p)_T \qquad (5a)$$

$$\beta^{(1)V} = (\partial\beta^{(1)}/\partial p)_T \qquad (5b)$$

$$2C^V = (\partial C^\phi/\partial p)_T \qquad (5c)$$

where C^ϕ is the third virial parameter for the osmotic coefficient.

Review of Literature Data

A number of investigators have measured the density of NaOH(aq) at 0.1 MPa in the temperature range from 273.15 to 348.15 K. Akerlof and Kegeles (6), Hitchcock and McIlhenny (7), and Hayward and Perman (8) measured densities with borosilicate glass pycnometers. Millero, Hoff, and Kahn (9) measured $\rho - \rho_0$ with a magnetic-float densimeter. Hershey, Damesceno, and Millero (10), Allred and Woolley (11), and Roux, Perron, and Desnoyers (12) have measured $\rho - \rho_0$ using vibrating tube densimeters, and Herrington, Pethybridge, and Roffey (13) reported densities obtained with a titanium dilatom-

eter. For consistent incorporation into the set of results used in the data analysis, reported densities or density differences were converted to V_ϕ values by use of eq 1 and the equation of state for water of reference 1. Weights were assigned to the V_ϕ values based on the estimated uncertainty of the experimental values propagated through eq 1.

A series of isothermal least-squares fits of eq 2 to the data was carried out as a check of the consistency of the various sets of results. The ion interaction treatment has the form of a virial equation in the interaction parameters, with corresponding limitations to its application at very high molalities, and was applied only to those results below 8.5 mol·kg⁻¹. The more recent studies show good internal precision in the dependence of V_ϕ on molality; the differences between sets of results are often significantly larger than the apparent uncertainties in a given set of values, particularly at low molalities. These differences lead to variation of as much as ±2 cm³·mol⁻¹ in values of $\bar{V}°_2$ calculated by extrapolation of the individual sets of results to infinite dilution. Results of the more recent studies, including this work, were weighted according to the estimated uncertainty in the reported values. The older data of ref 6–8 were given reduced weight in the analysis due to observed systematic differences in V_ϕ values as discussed below.

The variation with temperature of V_ϕ was accounted for by assigning a temperature dependence to the parameters of eq 2:

$$Q = u_{1,Q} + u_{2,Q}/(T - 227) + u_{3,Q}T + u_{4,Q}T^2 \qquad (6)$$

where Q is $\bar{V}°_2$, $\beta^{(0)V}$, $\beta^{(1)V}$, or $2C^V$ and the $u_{i,Q}$ are adjustable parameters. Values of the optimized parameters are listed in Table II. Rogers and Pitzer (2) found that the $\beta^{(1)V}$ parameter was not needed in their analysis of the volumetric data for NaCl(aq). Pabalan and Pitzer (4) also found that this parameter was not necessary in their recent treatment of the results for NaOH(aq). Here the coefficient was found to be defined statistically and was retained.

A series of plots of the residuals of fitting V_ϕ values with eq 2 and 6 are shown at various temperatures in Figure 1. The standard error of the fit was 0.2 cm³·mol⁻¹, with most of this error due to disagreement of the various sets of results rather than lack of precision of a given set of values or a systematic deviation in the fit. The data of Millero, Hoff, and Kahn (9) and of Hershey, Damesceno, and Millero (10), which show excellent internal precision and extend below 0.1 mol·kg⁻¹, should essentially determine the values of $\bar{V}°_2$ at the temperatures studied by these workers. The residual plots of Figure 1 show that these values extrapolate to significantly different intercepts from other sets of results except at 298.15 and 308.15 K. A plot against temperature of $\bar{V}°_2$ values determined from isothermal fits of the data of ref 9 and 10 show a much sharper maximum at lower temperature (near 318 K) than is consistent with the results at higher temperatures, and show deviations of about 1 cm³·mol⁻¹ from a smooth temperature dependence. These low concentration values have been retained in the data analysis, although the reason for the systematic deviation of these results from other studies is not clear.

Values of V_ϕ taken from Akerlof and Kegeles (6) show systematic differences from the more recent sets of results. The results of Hitchcock and McIlhenny (7) and of Hayward and Perman (8) are somewhat more scattered than those of Akerlof and Kegeles but have a similar systematic behavior in the fit residuals. These older sets of values were retained in the recent fit of Pabalan and Pitzer (4), but the reported standard fit deviations were large. The temperature range of interest is much smaller in the present study, and the molality range has been limited in an effort to obtain the most accurate representation consistent with the body of results available. Thus the older results, all carried out in corrodible borosilicate glass
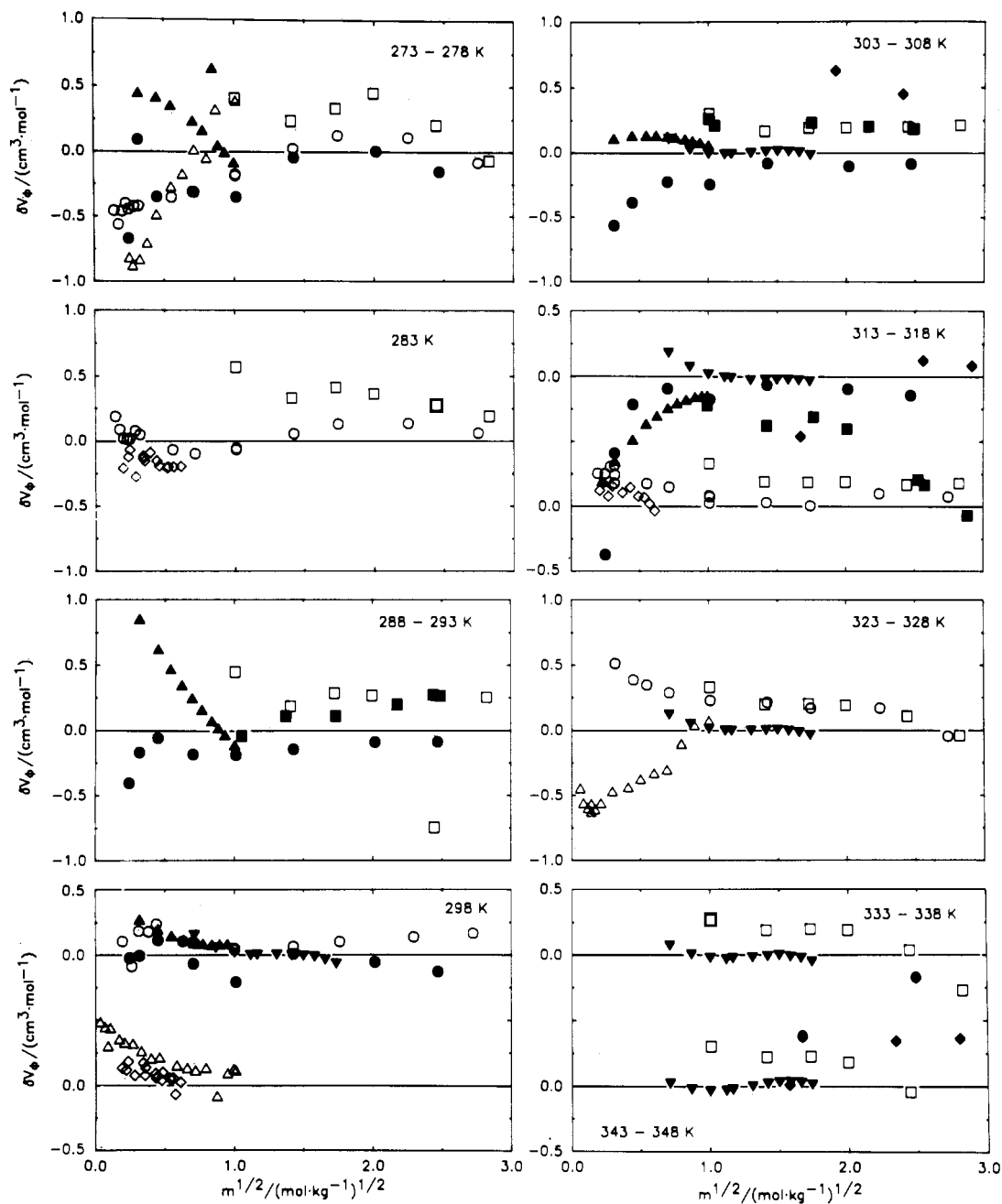
Figure 1. Fit residuals $\delta V_\phi = V_\phi$(calcd) $- V_\phi$(obsd) from fit of 0.1-MPa results to eq 2 at temperatures shown. ●, this study; ○, ref *12*; ▲, ref *10*; ▼, ref *13*; △, ref *9*; ◇, ref *11*; □, ref *6*; ■, ref *7*; ◆, ref *8*.

pycnometers, have been given reduced weights in this analysis.

It is apparent from Figure 1 that the internal precision of the experimental results of this study is not as good as that of some of the other recent studies. This increased scatter in the results may be attributed at least in part to difficulties in controlling the temperature of the vibrating tube cell using a circulating water bath.

For solution densities near 1 g·cm⁻³ the error in the relative density $\delta\rho$ is approximated by

$$\delta\rho = \delta V_\phi/(40 + 1000/m) \tag{7}$$

The largest errors in the relative density are near ±1000 ppm; this maximum is in the range of 3–6 mol·kg⁻¹ at all temperatures. Within this level of accuracy, specific volumes of NaOH(aq) calculated from the fitted V_ϕ results are listed in Table III.

Results at High Molalities

Values of V_ϕ obtained in this study extend to near 25 mol·kg⁻¹; Akerlof and Kegeles (*6*), Hayward and Perman (*7*), Hitchcock and McIlhenny (*8*), and Roux et al. (*12*) also report results above 8 mol·kg⁻¹. The ion interaction treatment may be extended to include higher power terms in the molality, as demonstrated in the work of Holmes et al. (*14*) and of Anathaswamy and Atkinson (*15*) in modeling the thermodynamic properties of HCl(aq) and CaCl₂(aq), respectively, to high ionic strengths. In the present case, this extension of the model is less satisfactory. The tendency of high-order power series to oscillate through a set of results is well-known. Most of the available densities at high molalities were determined in those studies which show a systematic deviation from the fit reported above; also, the results of this work are relatively widely spaced in molality above 8 mol·kg⁻¹. To avoid adversely affecting the

fit of results at lower molalities, a different empirical equation has been used to represent the volumetric results at high molalities. Akerlof and Kegeles (6) noted that their values of V_ϕ could be represented with a simple linear dependence on $m^{1/2}$, with different slopes at high and low molalities at a given temperature. A similar approach has been adopted here, where V_ϕ values at high molalities have been fitted to an arbitrary power series in $m^{1/2}$. Least-squares fits of the data from 8 to 25 mol·kg^{-1} showed that the linear dependence on $m^{1/2}$ gave systematic curvature in the fit residuals. This curvature was greatly reduced by assuming a dependence of V_ϕ on molality at high molalities given by

$$V_\phi = z_1 + z_2 m^{1/2} + z_3 m \qquad (8)$$

where the parameters z_i are functions of temperature:

$$z_i = a_i + b_i T + c_i/(T - 227) \qquad (9)$$

The systematic difference between sets of results has been discussed above. Given these differences, the results of ref 6-8 have again been given reduced weight in the least-squares analysis. Thus the parameters of eq 8 and 9 are determined almost completely by the results reported here and the highest molality points of Roux, Perron, and Desnoyers (12); eq 8 is therefore valid only from 278 to 318 K at molalities from 8 to 25 mol·kg^{-1}. No attempt has been made to force agreement of the V_ϕ values at 8 mol·kg^{-1} calculated from the two fitting equations. Agreement of V_ϕ calculated from eq 2 and 8 is within ±0.2 cm^3·mol^{-1} at 8 mol·kg^{-1}, giving values of the specific volume calculated from the two fits approximately within the fitting uncertainty of the lower molality treatment. The standard error of fit of the results at high molalities was 0.27 cm^3·mol^{-1}; noting this higher error of fit of the available data, the last digit in the tabulated specific volumes of NaOH(aq) at 0.1 MPa from 8 to 25 mol·kg^{-1} calculated from eq 8 is not significant.

Results at Higher Pressures. Compressibilities

The speed of sound in NaOH(aq) has been measured to 1 mol·kg^{-1} in the temperature range of interest by Hershey et al. (10), and Roux et al. (12) reported values at 298.15 K. The apparent molar compressibility κ_ϕ of these solutions is given by

$$\kappa_\phi = -(\partial V_\phi/\partial p)_T = 1000(\beta\rho_0 - \beta_0\rho)m\rho\rho_0 + \beta M_2/\rho \qquad (10)$$

where β and β_0 are the isothermal compressibilities $(1/\rho) \times (\partial\rho/\partial p)_T$ for NaOH(aq) and pure water. The adiabatic compressibility β_s is related to the speed of sound ω through

$$\beta_s = 1/(\omega^2\rho) \qquad (11)$$

and to the isothermal compressibility by

$$\beta = \beta_s + \alpha_T^2 T/\rho c_p \qquad (12)$$

where $\alpha_T = (-1/\rho)(\partial\rho/\partial T)_p$ and c_p is the specific heat capacity of the solution. Values of β_0, α_0, and ω_0 for water were calculated from the equation of Haar, Gallagher and Kell (1). The speed of sound in NaOH(aq) was calculated from measurements reported (10, 12) as differences in the speed of sound between NaOH(aq) and water $\Delta\omega = \omega - \omega_0$.

The required values of the specific heat capacity were obtained by fitting the appropriate form of the ion interaction treatment to the apparent molar heat capacities $C_{p,\phi}$ reported by Roux et al. (12) and by Allred and Woolley (11).

$$C_{p,\phi} =$$
$$\bar{C}_p{}^\circ{}_2 + \nu|z_M z_X|A_J h(I) + 2\nu_M\nu_X RT[mB^J + m^2(\nu_M z_M)C^J] \qquad (13)$$

In eq 13, B^J is related to the adjustable parameters for the

apparent molar heat capacity $\beta^{(0)J}$ and $\beta^{(1)J}$ as given for B^V in eq 4. The parameters $\bar{C}_p{}^\circ{}_2$, $\beta^{(0)J}$, $\beta^{(1)J}$, and C^J were assigned the temperature dependence given in eq 6; values of these parameters determined by fits of the data through 6 mol·kg^{-1} are given in Table IV. The standard error of fit of the apparent molar heat capacities was 1.5 J·K^{-1}·mol^{-1}.

Approximate values of κ_ϕ were calculated from the results reported here by averaging the finite differences $\Delta V_\phi/\Delta p$ for the 0.7–20.6-, 0.7–34.4-, and 20.6–34.4-MPa pressure intervals. Two equations were used to represent the molality dependence of κ_ϕ. In this case the ion interaction model was used over the range 0–6.5 mol·kg^{-1}, and the arbitrary power series in $m^{1/2}$ was fitted to the results at higher molalities. The appropriate equation for the ion interaction treatment is

$$\kappa_\phi =$$
$$\bar{\kappa}^\circ{}_2 - \{\nu|z_M z_X|A_K h(I) + 2\nu_M\nu_X RT[mB^K + m^2(\nu_M z_M)C^K]\} \qquad (14)$$

where $A_K = (\partial A_V/\partial p)_T$, $B^K = (\partial B^V/\partial p)_T$, $C^K = (\partial C^V/\partial p)_T$, and $\bar{\kappa}^\circ{}_2 = -(\partial\bar{V}^\circ{}_2/\partial p)_T$. Each of the composition-independent parameters of eq 14 was assigned the temperature dependence given by eq 6. In this case the second pressure derivative of the $\beta^{(1)}$ parameter was not needed to represent the compressibilities. Temperature-independent parameters needed to calculate the coefficients of eq 14 are given in Table V.

Values of the parameters of the corresponding form of eq 8

$$\kappa_\phi = k_1 + k_2 m^{1/2} + k_3 m \qquad (15)$$

were obtained by fitting the apparent molar compressibilities above 6.5 mol·kg^{-1}; the temperature dependence of the k_i is given by eq 9. The parameters needed to calculate k_i at the temperature of interest are given in Table V. As with the piecewise definition of the molality dependence of the apparent molar volume, no attempt has been made to force agreement of the values or composition derivatives of κ_ϕ into agreement near the changeover composition (6.5 mol·kg^{-1}). Inspection of the plots of κ_ϕ against $m^{1/2}$ at various temperatures in Figure 2 illustrates that there are no large differences in value or slope of κ_ϕ in the crossover region. A representative portion of the κ_ϕ values calculated from the sound speed data of Hershey et al. (10) are also shown in Figure 2; values calculated from the sound speeds measured at 298.15 K by Roux et al. (12) are in excellent agreement with those of ref 10.

The apparent molar compressibilities are assumed independent of pressure over the range considered here, leading to the expression for V_ϕ as a function of pressure:

$$V_\phi(p) = V_\phi(0.1 \text{ MPa}) - (p - 0.1)\kappa_\phi \qquad (16)$$

Specific volumes of NaOH(aq) at 20.0 and 40.0 MPa calculated from eq 16 and the appropriate equations for V_ϕ and κ_ϕ are given in Table III.

Discussion

One of the purposes of treating experimental volumetric results at finite molalities with a model which includes the electrostatic limiting law with other terms needed at higher molalities is to extract values of the standard state properties. Calculated values of $\bar{V}^\circ{}_2$, $\bar{E}^\circ{}_2$, and $\bar{\kappa}^\circ{}_2$ at 0.1 MPa are listed in Table VI, where $\bar{E}^\circ{}_2$ is the standard-state partial molar expansivity. The values of $\bar{\kappa}^\circ{}_2$ were determined here by fitting eq 14 to the κ_ϕ calculated from the results of Hershey, Damesceno, and Millero (10) and from Roux, Perron, and Desnoyers (12), with corresponding very good agreement of the values of Table VI with those given in ref 10 and with the value at 298.15 K of -7.88 cm^3·MPa^{-1}·mol^{-1} obtained by Mathieson and Conway (16). $\bar{E}^\circ{}_2$ has been reported at 283.15, 298.15, and 313.15 K by Roux

Table II. Fitting Parameters for the Apparent Molar Volume of NaOH(aq)

Eq 6: 0-8.5 m, 278.15-348.15 K, 0.1 MPa

Q	$\bar{V}^0_2$/(cm³·mol⁻¹)	$\beta^{(0)V}$/(kg·mol⁻¹·MPa⁻¹)	$\beta^{(1)V}$/(kg·mol⁻¹·MPa⁻¹)	$2C^V$/(kg²·mol⁻²·MPa⁻¹)
u_1	-47.2184	-3.24287 × 10⁻⁵	3.79568 × 10⁻³	-1.16142 × 10⁻⁴
u_2	-445.889	1.83077 × 10⁻²		
u_3	0.314497		-1.04928 × 10⁻⁵	3.45044 × 10⁻⁷
u_4	-5.16093 × 10⁻⁴			

Eq 9: 8.5-25.0 m, 278.15-318.15 K, 0.1 MPa

	z_1/(cm³·mol⁻¹)	z_2/(cm³·kg^{1/2}·mol^{-3/2})	z_3/(cm³·kg·mol⁻²)
a_k	-18.1055	8.80773	-0.489378
b_k	0.0271532	-5.75276 × 10⁻³	
c_k	-74.2286		

Table III. Specific Volumes of NaOH(aq)

T/K	molality/(mol·kg⁻¹)																	
	0.1	0.25	0.5	1.0	2.0	3.0	4.0	5.0	6.0	8.0	10.0	12.0	14.0	16.0	18.0	20.0	22.0	25.0
	p = 0.1 MPa																	
273.15	0.9953	0.9883	0.9771	0.9563	0.9196	0.8884	0.8615	0.8383	0.8182	0.7849	0.7551	0.7317	0.7123	0.6959	0.6819	0.6699	0.6593	0.6457
283.15	0.9956	0.9889	0.9781	0.9580	0.9224	0.8917	0.8650	0.8417	0.8211	0.7864	0.7578	0.7347	0.7154	0.6992	0.6853	0.6733	0.6627	0.6492
293.15	0.9973	0.9907	0.9802	0.9606	0.9256	0.8953	0.8687	0.8453	0.8245	0.7892	0.7610	0.7379	0.7187	0.7024	0.6885	0.6765	0.6659	0.6522
298.15	0.9985	0.9920	0.9816	0.9622	0.9274	0.8972	0.8707	0.8472	0.8264	0.7910	0.7627	0.7397	0.7204	0.7041	0.6902	0.6781	0.6675	0.6537
303.15	0.9999	0.9935	0.9832	0.9639	0.9293	0.8992	0.8727	0.8492	0.8284	0.7930	0.7645	0.7415	0.7222	0.7059	0.6919	0.6797	0.6690	0.6552
313.15	1.0035	0.9971	0.9869	0.9677	0.9334	0.9033	0.8768	0.8533	0.8325	0.7974	0.7685	0.7453	0.7259	0.7095	0.6954	0.6831	0.6722	0.6581
323.15	1.0078	1.0014	0.9913	0.9722	0.9378	0.9076	0.8811	0.8577	0.8369	0.8023	0.7728	0.7495	0.7300	0.7134	0.6991	0.6866	0.6756	0.6612
333.15	1.0127	1.0064	0.9962	0.9771	0.9425	0.9123	0.8856	0.8622	0.8416	0.8076								
343.15	1.0184	1.0120	1.0018	0.9825	0.9477	0.9172	0.8904	0.8669	0.8464	0.8133								
	p = 20.0 MPa																	
273.15	0.9858	0.9791	0.9685	0.9487	0.9135	0.8831	0.8569	0.8340	0.8141	0.7819	0.7525	0.7295	0.7102	0.6939	0.6800	0.6679	0.6573	0.6437
283.15	0.9866	0.9802	0.9699	0.9507	0.9164	0.8866	0.8606	0.8377	0.8175	0.7835	0.7554	0.7326	0.7135	0.6973	0.6834	0.6714	0.6610	0.6474
293.15	0.9886	0.9823	0.9723	0.9534	0.9197	0.8902	0.8643	0.8414	0.8210	0.7864	0.7585	0.7358	0.7167	0.7005	0.6867	0.6747	0.6642	0.6506
298.15	0.9899	0.9837	0.9737	0.9550	0.9215	0.8921	0.8662	0.8432	0.8229	0.7881	0.7602	0.7374	0.7184	0.7022	0.6883	0.6763	0.6657	0.6521
303.15	0.9914	0.9853	0.9754	0.9567	0.9233	0.8940	0.8681	0.8451	0.8248	0.7900	0.7619	0.7391	0.7200	0.7038	0.6899	0.6779	0.6673	0.6535
313.15	0.9950	0.9889	0.9791	0.9606	0.9273	0.8980	0.8721	0.8491	0.8287	0.7942	0.7657	0.7428	0.7236	0.7073	0.6933	0.6811	0.6704	0.6565
323.15	0.9993	0.9932	0.9834	0.9649	0.9316	0.9022	0.8763	0.8533	0.8329	0.7988	0.7697	0.7467	0.7274	0.7109	0.6968	0.6844	0.6736	0.6594
	p = 40.0 MPa																	
273.15	0.9768	0.9705	0.9605	0.9416	0.9078	0.8785	0.8527	0.8302	0.8104	0.7794	0.7504	0.7276	0.7085	0.6923	0.6783	0.6662	0.6557	0.6420
283.15	0.9781	0.9720	0.9623	0.9439	0.9109	0.8821	0.8566	0.8342	0.8143	0.7811	0.7534	0.7308	0.7118	0.6957	0.6819	0.6699	0.6594	0.6459
293.15	0.9804	0.9744	0.9648	0.9467	0.9142	0.8856	0.8602	0.8378	0.8179	0.7839	0.7565	0.7339	0.7150	0.6989	0.6851	0.6732	0.6627	0.6491
298.15	0.9818	0.9759	0.9663	0.9483	0.9159	0.8874	0.8621	0.8396	0.8197	0.7856	0.7581	0.7355	0.7166	0.7005	0.6867	0.6747	0.6642	0.6507
303.15	0.9834	0.9775	0.9680	0.9501	0.9177	0.8892	0.8639	0.8415	0.8215	0.7874	0.7597	0.7372	0.7182	0.7021	0.6883	0.6763	0.6658	0.6521
313.15	0.9870	0.9812	0.9717	0.9539	0.9216	0.8931	0.8678	0.8453	0.8252	0.7913	0.7632	0.7406	0.7215	0.7054	0.6915	0.6794	0.6688	0.6550
323.15	0.9913	0.9854	0.9760	0.9581	0.9258	0.8972	0.8718	0.8493	0.8293	0.7957	0.7669	0.7442	0.7251	0.7088	0.6948	0.6826	0.6718	0.6580

Table IV. Fitting Parameters for the Apparent Molar Heat Capacity of NaOH(aq)

Eq 13: 0–6.0 m, 278.15–328.15 K, 0.1 MPa

Q	$\bar{C}_{p}^{\circ}{}_{2}/$ (J·K^{-1}·mol^{-1})	$\beta^{(0)J}/$ (kg·K^{-2}·mol^{-1})	$\beta^{(1)J}/$ (kg·K^{-2}·mol^{-1})	$2C^{J}/$ (kg^2·K^{-2}·mol^{-2})
q_1	3.14595 × 10^3	1.16508 × 10^{-3}	1.68895 × 10^{-3}	−3.24698 × 10^{-4}
q_2	−3.58904 × 10^4	−6.35167 × 10^{-3}	−3.24273 × 10^{-2}	1.60831 × 10^{-3}
q_3	−1.43654 × 10^1	−6.60292 × 10^{-6}	−4.22279 × 10^{-6}	1.82581 × 10^{-6}
q_4	1.73497 × 10^{-2}	9.81818 × 10^{-9}		−2.69073 × 10^{-9}

Table V. Fitting Parameters for the Apparent Molar Compressibility of NaOH(aq)

Eq 14: 0–6.5 m, 273.15–323.15 K

Q	$\bar{\kappa}^{\circ}{}_{2}/(\text{cm}^3\cdot\text{MPa}^{-1}\cdot\text{mol}^{-1})$	$\beta^{(0)K}/(\text{cm}^3\cdot\text{kg}\cdot\text{MPa}^{-2}\cdot\text{mol}^{-1})$	$2C^{K}/(\text{cm}^3\cdot\text{kg}^2\cdot\text{MPa}^{-2}\cdot\text{mol}^{-2})$
u_1	−1.38604	1.01784 × 10^{-6}	1.90754 × 10^{-6}
u_2	−9.39619 × 10^{-1}	−2.20494 × 10^{-4}	
u_3	8.16550 × 10^{-3}		−5.50920 × 10^{-9}
u_4	−1.25354 × 10^{-5}		

Eq 15: 6.5–25 m, 273.15–323.15 K

	$k_1/(\text{cm}^3\cdot\text{MPa}^{-1}\cdot\text{mol}^{-1})$	$k_2/(\text{cm}^3\cdot\text{kg}^{1/2}\cdot\text{MPa}^{-1}\cdot\text{mol}^{-3/2})$	$k_3/(\text{cm}^3\cdot\text{kg}\cdot\text{MPa}^{-1}\cdot\text{mol}^{-2})$
a_k	−2.37890 × 10^{-1}	5.56269 × 10^{-2}	−2.34474 × 10^{-3}
b_k	4.96112 × 10^{-4}	−9.42947 × 10^{-5}	

Table VI. Standard-State Volumetric Properties for NaOH(aq) at 0.1 MPa

$T/$K	$\bar{V}^{\circ}{}_{2}/$ (cm^3·mol^{-1})	$10^2\bar{E}^{\circ}{}_{2}/$ (cm^3·K^{-1}·mol^{-1})	$10^2\bar{\kappa}^{\circ}{}_{2}/$ (cm^3·MPa^{-1}·mol^{-1})
278.15	−8.387	19.8	−10.3
288.15	−6.739	13.6	−8.93
298.15	−5.595	9.48	−7.90
308.15	−4.807	6.41	−7.17
318.15	−4.292	3.98	−6.73
328.15	−3.999	1.94	
338.15	−3.896	0.16	
348.15	−3.962	−1.45	

et al. and may be calculated at various temperatures by differentiation of the equations for $\bar{V}^{\circ}{}_{2}$ given by Hershey et al. and by Pabalan and Pitzer (*4*). The values calculated from the treatment given here agree within 1.5 cm^3·K^{-1}·mol^{-1} with those of Pabalan and Pitzer through 318.15 K, with the difference increasing to 3.5 cm^3·K^{-1}·mol^{-1} at 348.15 K. Agreement with the values given by Roux et al. is excellent at 298.15 and 313.15 K and within 5 cm^3·K^{-1}·mol^{-1} at 283.15 K. Differentiation with temperature of the two equations for $\bar{V}^{\circ}{}_{2}$ given by Hershey et al. gives $\bar{E}^{\circ}{}_{2}$ higher than those in Table VI by more than a factor of 2 at 278.15 K, with better agreement at higher temperatures. This difference is clearly due to the larger negative values of $\bar{V}^{\circ}{}_{2}$ at low temperatures obtained by Hershey et al.

The $\bar{V}^{\circ}{}_{2}$ values reported by various investigators fall within a range of about ±1 cm^3·mol^{-1} over the temperature range considered here. Agreement of the $\bar{V}^{\circ}{}_{2}$ of Table VI with those calculated by Allred and Woolley (*11*) at 283.15, 298.15, and 313.15 K is within ±0.2 cm^3·mol^{-1}; at 298.15 K $\bar{V}^{\circ}{}_{2}$ of Table VI is 0.35 cm^3·mol^{-1} more negative than the value given by Hepler, Stokes, and Stokes (*17*). The values reported here are more negative at all temperatures than those calculated by Herrington et al. (*13*), with a difference of about 0.7 cm^3·mol^{-1}. The residuals of fitting the results of ref *13* were never as large as the differences in $\bar{V}^{\circ}{}_{2}$; the small fit errors to these data coupled with the relatively high lower molality limit of the results (0.5 m) lead to the noted difference in the standard-state volume. The intercepts calculated by Roux, Perron, and Desnoyers (*12*) cut through the present set of values, being more negative by 0.4 cm^3·mol^{-1} at 277.15 K and 0.6 cm^3·mol^{-1} less negative at 313.15 K. The large differences in $\bar{E}^{\circ}{}_{2}$ determined in this study from those calculated from the treatment of Hershey, Damesceno, and Millero (*10*) are reflected in the stand-
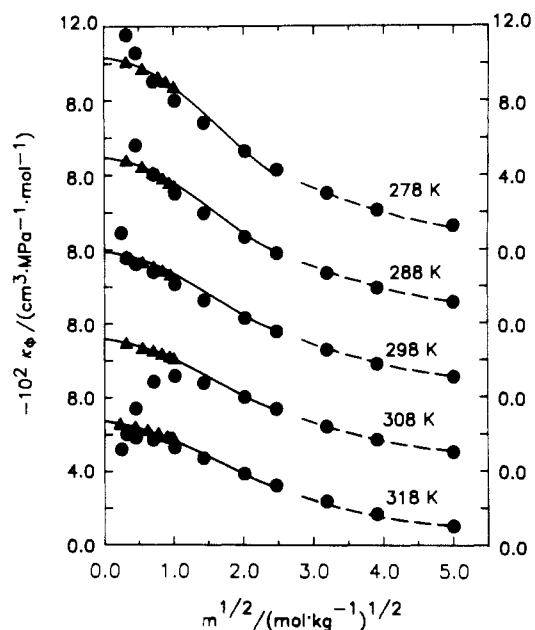

Figure 2. Apparent molar compressibilities from ▲, ref *10*; ●, this study. Solid curves calculated from eq 14; dashed curves calculated from eq 15.

ard-state volumes, where the volumes of ref *10* are about 1 cm^3·mol^{-1} more negative at 273.15 and 348.15 K and 0.8 cm^3·mol^{-1} higher at 298.15 K. The present values lie about 0.5 cm^3·mol^{-1} below those calculated by Pabalan and Pitzer from 273.15 to 308.15 K, but do not drop as steeply at higher temperatures, and are less negative by 0.3 cm^3·mol^{-1} at 348.15 K. On the basis of the differences between sets of results as described above, the accuracy of $\bar{V}^{\circ}{}_{2}$ at 0.1 MPa in this temperature range is estimated to be ±0.5 cm^3·mol^{-1}.

One application for the standard-state values detailed above is in calculating reaction thermodynamic properties in aqueous solution. Standard-state properties of NaOH(aq) may be combined with those for NaCl(aq), HCl(aq), and H$_2$O to give the reaction thermodynamics for the ionization of water

$$\Delta Y^{\circ} = \bar{Y}^{\circ}{}_{2}(\text{NaOH}) + \bar{Y}^{\circ}{}_{2}(\text{HCl}) - \bar{Y}^{\circ}{}_{2}(\text{NaCl}) - Y^{\circ}(\text{H}_2\text{O}) \tag{17}$$

In the present case, the ΔY° for $Y = V$, E, κ, and C_p may be calculated from eq 17 and the results of this study for

NaOH(aq), combined with those of Haar et al. (*1*) for H_2O, Pitzer, Peiper, and Busey (*18*) for NaCl(aq) and Hershey et al. (*10*) and Holmes et al. (*14*) for HCl(aq). $\Delta V°$ and $\Delta C_p°$ calculated from eq 17 at 273.15, 298.15, and 323.15 K agree with those given by Sweeton, Baes, and Mesmer (*19*) within their estimated uncertainties, except for $\Delta C_p°$ at 298.15 K where the calculated value of -213.6 $J \cdot K^{-1} \cdot mol^{-1}$ compares with a value of -231 ± 6 from Sweeton et al. These authors included results over a very wide temperature range (to 573.15 K), and the more recent heat capacity results were not available at the time of their analysis; these factors result in the relatively large discrepancy noted at 298.15 K. The $\Delta V°$ of -22.51 $cm^3 \cdot mol^{-1}$ calculated from eq 17 at 298.15 K and the heat capacity change given above are in good agreement with the values $\Delta C_p° = -215$ $J \cdot K^{-1} \cdot mol^{-1}$ and $\Delta V° = -22.10$ $cm^3 \cdot mol^{-1}$ selected in the critical review of Hepler and Hopkins (*20*). Given the very close agreement of $\bar{\kappa}°_2$ values of this work with those of Hershey et al., the differences in $\Delta \kappa°$ calculated from the two representations for the NaOH(aq) properties are negligible. Taking into account the relatively large uncertainties estimated for the standard-state properties calculated from the treatment reported here, the more important contribution of the present study is in the measured values at high concentrations rather than as a source of significantly improved values of standard-state thermodynamic properties.

Acknowledgment

Glossary

a_k, b_k, c_k	temperature-independent fit parameters for power series
b	parameter of ion interaction model
c_p	specific heat capacity at constant pressure
k_i, z_i	molality-independent parameters of power series fit
m	solution molality
p	pressure in MPa
u_i	temperature-independent fit parameters of ion interaction model
A_V, A_K	limiting slopes for apparent molar volume and compressibility
C^ϕ, B^V, C^V, B^J, C^J, B^K, C^K	ion interaction coefficients
E	expansivity
I	ionic strength
V_ϕ, $C_{p,\phi}$, κ_ϕ	apparent molar volume, heat capacity, compressibility
$\bar{V}°_2$, $\bar{C}_{p}°_2$, $\bar{\kappa}°_2$	standard-state partial molar volume, heat capacity, compressibility
α	parameter of ion interaction model
α_T	solution thermal expansion coefficient
$\beta^{(0)}$, $\beta^{(1)}$	molality-independent coefficients of ion interaction model
β, β_s	isothermal and adiabatic compressibility coefficients
δV_ϕ	fit residual V_ϕ(calcd) – V_ϕ(obsd)
ρ, ρ_0	densities of solution and water
ω, ω_0	speed of sound in solution and in water

Registry No. NaOH, 1310-73-2.

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