Thermodynamics of Aqueous NaOH over the Complete Composition Range and to 523 K and 400 MPa

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The thermodynamic properties of aqueous NaOH are represented for the entire range to extremely high concentration by mole fraction based equations. The apparent molar volume and the solvent and solute activities are obtained from literature values based on experimental measurements extending over the ranges 273−523 K and 0−400 MPa. For the range below 6 mol kg^{-1} the values from the very comprehensive treatment of Simonson et al. are given high weight. At the highest temperature the dissociated mole fraction of NaOH extends to 0.9. The equations represent the data satisfactorily over this very wide range and are of a form readily extended to more complex mixed systems and to solubility calculations.

I. Introduction

Sodium hydroxide is completely miscible in water to pure liquid NaOH above 595 K and is soluble to very high concentration at lower temperatures. Thus, an equation representing its behavior over the full range of composition must be on a mole-fraction rather than a molality basis. Since NaOH(aq) is a strong electrolyte to at least 573 K, the fully ionized basis is appropriate for that range. Equations of this type combining a Debye−Hückel term with Margules terms have now been used successfully for several systems.[1−11] The range of experimental data for NaOH−H$_2$O to 523 K and 400 MPa is exceptionally extensive; thus, it is a challenge to provide an accurate representation in a form that also allows convenient application to multicomponent systems. The form of equation presented by Clegg and Pitzer[7] and Clegg et al.[8] is appropriate for NaOH−H$_2$O and is designed for convenient extension to three or more components. Indeed, a subsequent publication will treat several such systems with additional solutes, together with NaOH. Equilibria with solid phases will be considered as well as the properties of the liquid phase.

For aqueous NaOH at moderate concentrations, Simonson et al.[12] reported new measurements of heats of dilution and heat capacities, and presented a comprehensive treatment to 523 K on a molality basis valid to about 6 mol kg^{-1}. An earlier treatment of Pabalan and Pitzer[13] extended to 623 K and 10 mol kg^{-1} but was superseded by the Simonson treatment for lower molalities and lower temperatures up to 523 K. Citations of earlier studies of aqueous NaOH are given in refs 12 and 13.

Initially, a single equation for the full range to 623 K was sought, but it became extremely complex if full accuracy was retained at all temperatures. Thus, we decided to limit the present treatment to 523 K. We hope to present a second equation valid from 423 to 623 K in the near future.

II. Theory

The mole fraction on a fully dissociated basis but limited to a single symmetrical (MX) solute is given by

$$x_1 = n_1/(n_1 + 2n_2) \tag{1a}$$

$$x_2 = 2n_2/(n_1 + 2n_2) \tag{1b}$$

where n_1 and n_2 refer to moles of water and solute (MX), respectively, and x_1 and x_2 correspondingly are the mole fractions on the ionized basis. The ionic strength is then

$$I_x = {}^1\!/_2 \sum x_i z_i^2$$

and with $x_i = x_2/2$ and z_i the ion charge. For NaOH with $z_i^2 = 1$,

$$I_x = x_2/2 \tag{2}$$

The definitions of ideal mixing terms and the excess Gibbs energy were thoroughly examined by Pitzer and Simonson[2] for the fully dissociated ionic system using mole fraction based equations. The ideal Gibbs energy of mixing is

$$\Delta_m G^I/RT = \sum n_i \ln(x_i/x_i^0) \tag{3a}$$

$$= n_1 \ln x_1 + 2n_2 \ln x_2 \tag{3b}$$

The choice $x_1^0 = 1$ for the solvent is straightforward, and for each solute ion $x_i = x_2/2$, but $x_i^0 = {}^1\!/_2$; hence, the simple result in eq 3b. Then the excess Gibbs energy is

$$G^E = \Delta_m G - \Delta_m G^I \tag{4}$$

with $\Delta_m G$ the value for the formation of the real solution from the solute and solvent in their reference states. Activity coefficients are obtained by differentiation of the excess Gibbs energy.

$$\ln \gamma_i = \frac{1}{RT}\left(\frac{\partial G^E}{\partial n_i}\right)_{T,P,n_j \neq i} \tag{5}$$

The reference state of water is the pure liquid, but two options must be considered for the solute reference state. Usually, it is most convenient to use the "infinite dilution" reference state, which has $\ln \gamma_2 = 0$ at $x_2 = 0$ and represents an extrapolation of the properties as $x_2 \to 0$ on an ideal solution basis to $x_2 = 1$. The other option is the pure fused salt (possibly extrapolated from higher temperature) as the reference state. Then $\ln \gamma_2 = 0$ at $x_2 = 1.0$. G^E is zero at $x_2 = 0$ for either case, but it is zero at $x_2 = 1$ only for the "pure liquid" case.

It is convenient to use a dissociated molar basis for the Gibbs energy with

$$g = G/(n_1 + 2n_2) \tag{6}$$

$$\Delta_m g^I/RT = x_1 \ln x_1 + x_2 \ln x_2 \tag{7}$$

$$g^E = \Delta_m g - \Delta_m g^I \tag{8}$$

The most general formulation for the excess molar Gibbs energy for the system MX−H_2O, a 1−1 electrolyte, on an infinite dilution reference basis is

$$g^E/RT = -4(A_x/\rho)I_x \ln(1 + \rho I_x^{1/2}) + (x_2^2/4)[B_{MX}g(\alpha I_x^{1/2})] - x_2^2(W_{1,MX} - x_1 U_{1,MX} - x_1 x_2 V_{1,MX}) \tag{9}$$

$$g(y) = 2[1 - (1 + y)\exp(-y)]/y^2 \tag{10}$$

A_x is the Debye−Hückel parameter on a mole-fraction basis; it is

$$A_x = \Omega^{1/2}A_\phi \tag{11}$$

with A_ϕ the value in the equation for the osmotic coefficient on a molality basis and Ω the number of moles of solvent per kg, 55.51 for water. The parameter ρ is related to the "closest-approach" distance for the ions. While the value of ρ could be different for each solute, the choice of a single, fixed value greatly simplifies the equations for multicomponent systems. The B_{MX} term in eq 9 is related to the $\beta^{(1)}$ term in the molality-based equations, which was introduced to maintain good agreement with a fixed value of the closest-approach parameter b. The parameter B_{MX} is specific to each electrolyte MX. The value of α is large so that the exponential decreases rapidly with I_x. While α can be chosen separately for each solute, a standard value of 13 has been found to be satisfactory.[7−11] $I_x = x_2/2$ as given in eq 2.

The terms W and U are the Margules terms used generally in this type of equation, and V is just the next higher order term in that series.

Many successful applications of this type of equation have used only a few of the terms in eq 8. Thus, Simonson and Pitzer[4] treated $LiNO_3$−H_2O and KNO_3−H_2O over the full range to the fused salts using only three terms: the Debye-Hückel term and $W_{1,MX}$ and $U_{1,MX}$. But, they adjusted ρ. Clegg and Brimblecombe[14] used the same three-term basis for the full range 0−100% for nitric acid with a temperature-dependent ρ. Later, after adding the term B_{MX}, Clegg and others[7−11] have used $\rho = 13$ for several systems. We recommend the inclusion of the B_{MX} term for the future and the adoption of $\rho = 13$ as a standard value. Also, it appears that $\alpha = 13$ is satisfactory in most cases.

From eqs 5, 6, and 9 the equations for the activity coefficients for a 1−1 electrolyte are

$$\ln \gamma_1 = 2A_x I_x^{3/2}/(1 + \rho I_x^{1/2}) - (x_2^2/4)[B_{MX}\exp(-\alpha I_x^{1/2})] + x_2^2[W_{1,MX} + (x_2 - x_1)U_{1,MX} + x_1(2 - 3x_1)V_{1,MX}] \tag{12}$$

$$\ln \gamma_{\pm,x} = -A_x[(2/\rho)\ln(1 + \rho I_x^{1/2}) + I_x^{1/2}(1 - 2I_x)/(1 + \rho I_x^{1/2})] + (x_2/4)B_{MX}[g(\alpha I_x^{1/2}) + (1 - x_2)\exp(-\alpha I_x^{1/2})] + (x_1^2 - 1)W_{1,MX} + x_1^2 x_2[2U_{1,MX} + (2 - 3x_2)V_{1,MX}] \tag{13}$$

The symbol $\gamma_{\pm,x}$ is used to remind one that the solute activity coefficient on the mole-fraction basis differs from that on a molality basis. The activities are related to the activity coefficients as follows:

$$\ln a_1 = \ln x_1 + \ln \gamma_1 \tag{14}$$

$$\ln a_2 = 2 \ln x_2 + 2 \ln \gamma_{\pm,x} \tag{15}$$

The activity a_1 of water remains unchanged for a shift to the molality basis.

For convenience in calculations on a molality basis, we note the conversion relationships for a 1−1 electrolyte MX

$$x_\pm = x_M = x_x = \frac{x_2}{2} = \frac{m}{55.51 + 2m} \tag{16}$$

$$\gamma_{\pm,m} = \gamma_{\pm,x}/(1 + 0.03603m) \tag{17}$$

III. Volumetric Properties

For density and volumetric calculations the pressure derivative of the excess Gibbs energy yields the basic equation.

It is convenient to use the apparent molar volume

$$^\phi V = (V - n_1 V_i^0)/n_2 \tag{18}$$

with

$$V = (\partial G/\partial P)_{T,n_1,n_2} \tag{19}$$

and V_1^0, the molar volume of pure water.

For the representation of the volumetric properties of NaOH-(aq) the term in $V_{1,MX}$ was not needed; hence it is omitted in the equations in this section. From eqs 6, 9, 18, and 19 one obtains

$$^\phi V = \bar{V}_2^0 + (A_{V,x}/\rho)\ln(1 + \rho I_x^{1/2}) + (x_2/2)B_{MX}^V g(\alpha I_x^{1/2}) - 2x_2(W_{1,MX}^V - x_1 U_{1,MX}^V) \tag{20}$$

Equation 20 is for the infinite dilution reference state. For the volumetric calculations, we found it useful to use the pure fused liquid reference state. Substitution of $x_2 = 1$, $I_x = 1/2$, $x_1 = 0$ in eq 20 yields

$$V_2^{fus} = \bar{V}_2^0 + (A_{V,x}/\rho)\ln(1 + \rho/2^{1/2}) + (1/2)B_{MX}^V g(\alpha/2^{1/2}) - 2W_{1,MX}^V \tag{21}$$

and the apparent molar volume on the pure liquid basis is

$$^\phi V = V_2^{fus} + \left(\frac{A_{V,x}}{\rho}\right)\ln\left[\frac{1 + \rho I_x^{1/2}}{1 + \rho/2^{1/2}}\right] + (1/2)B_{MX}^V[x_2 g(\alpha I_x^{1/2}) - g(\alpha/2^{1/2})] + 2x_1(W_{1,MX}^V + x_2 U_{1,MX}^V) \tag{22}$$

The various volumetric parameters are pressure derivatives of the Gibbs energy parameters with modifying factors so that they have the dimension molar volume.
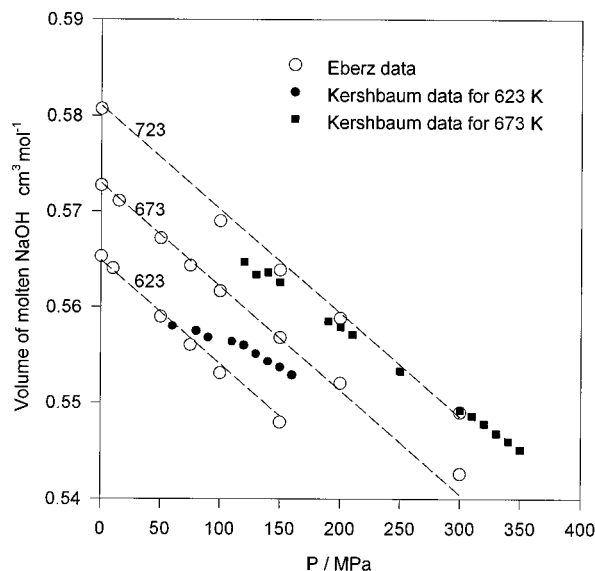
$$A_{V,x} = -4RT\Omega^{1/2}(\partial A_\phi/\partial P)_T \tag{23}$$

$$B_{MX}^V + RT(\partial B_{MX}/\partial P) \tag{24}$$

$$W_{1,MX}^V = RT(\partial W_{1,MX}/\partial P)_T \tag{25}$$

$$U_{1,MX}^V = RT(\partial U_{1,MX}/\partial P)_T \tag{26}$$

For W^V and U^V, the factor RT is a change from the definition used by Pabalan and Pitzer.[6]

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Figure 1. Volume of fused NaOH at different pressures and temperatures. The dashed lines show the linear approximation.

Figure 2. Apparent molar volume at saturation pressure and different temperatures. For convenience of representation, the curves were shifted $\Delta^\phi V = +10$ for 473 K, +20 for 423 K, +30 for 373 K, and +60 for 273 K.

Before fitting the data for solutions, it was desirable to consider the volume of fused NaOH. Data are available for 1 bar from Krey,[15] whose values agree with extrapolations of the data for extremely concentrated solutions from Krumgalz and Mashovets.[16]

Only two sources of V_2^{fus} at elevated pressure are available—the measurements of Eberz and Franck[17] and Kerschbaum and Franck.[18] We found that these two data sets are not consistent with each other. Thus, on Figure 1 one can see that data reported by Kerschbaum and Franck for 673 K are close to the Eberz and Franck results at 723 K. We decided to use Eberz results as the more reasonable. Also, they are in accordance with the 1 bar data of Krey.[14] Linear dependencies on T and P sufficed. The dashed lines in Figure 1 show the final fit

$$V_2^{fus} = 0.464\,086 + 0.000\,161\,748\,T - 1.085 \times 10^{-4}\,P \tag{27}$$

with T in K and P in MPa here and throughout.

There are numerous measurements of the density and apparent molar volume of aqueous NaOH. For values at saturation pressure, the very extensive results of Dibrov et al.[19,20] and of Krumgalz et al.[16] cover the full range to solid saturation or to fused NaOH. Krey[15] collected all volumetric data available to 1972 and made a polynomial fit. His results were very reasonable and were included. Roux et al.[21] report measurements of volumetric and thermal properties to 11 mol kg^{-1} at several temperatures from 4 to 55 °C. For relatively dilute solutions Corti et al.[22] report measurements from 100 to 250 °C.

There are three sources of volumetric data for solutions at higher than saturation pressure. Kerschbaum and Franck[18] and Eberz and Franck[17] cover a wide interval of pressures, up to 400 MPa, and concentrations, 5.11 wt % (Eberz) to 100 wt % at appropriate temperatures. Simonson and Ryther[23] measured apparent molar volumes up to 34.47 MPa and 317.48 K for the concentration range 0.06−25.02 molal.

Preliminary fits were made of the data at saturation pressure, which showed good agreement among the various sources and indicated the temperature dependency of the parameters. The following expression was selected for the temperature dependency of the parameters W^V, U^V, and B^V.

$$\text{PAR} = c_1 + c_2/T + c_3T + c_4/(647 - T) \tag{28}$$
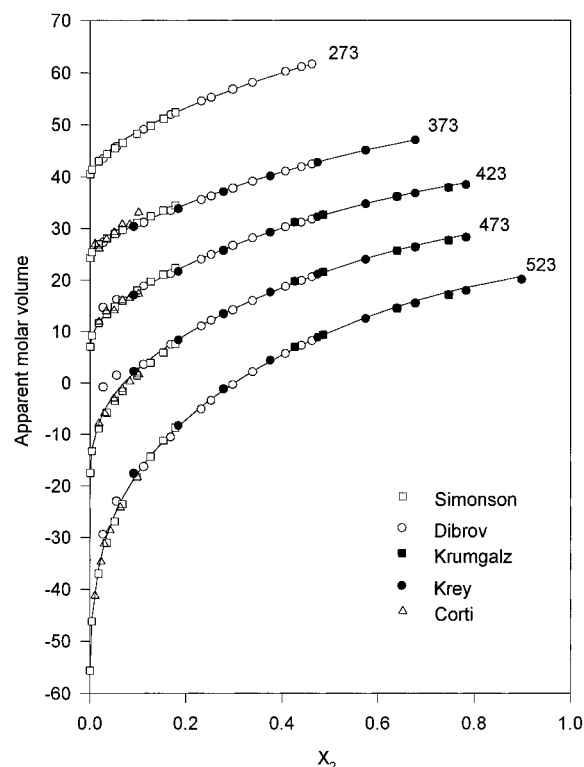
TABLE 1: Temperature Dependencies of Parameters at Saturation Pressure

|	c_1	c_2	c_3	c_4
$W_{1,MX}$	1.431	−1846	0.0	0.0
$U_{1,MX}$	−14.253	6949	0.0	0.0
B_{MX}	139.714	0.0	−0.278	0.0
$V_{1,MX}$	60.227	−17 913	−0.052	0.0
$W^V_{1,MX}$	38.98	−8485	−0.085	1309
$U^V_{1,MX}$	−27.60	6203	0.051	0.0
B^V_{MX}	−15 987	2 776 230	24.15	−148 446
V_2^0	211.7	−36 821	−0.213	−10 547

The coefficients c_1−c_4 are listed in Table 1, and examples of the fit are shown on Figure 2.

The molar volume V_2^0 at infinite dilution is given by eq 20, and values V_2^{fus}, $W^V_{1,MX}$, and B^V_{MX} were calculated using eqs 27 and 28 at the temperature of interest; the result is shown in Figure 3. For the convenience of the reader we have also expressed V_2^0 in the form of eq 28 and added it to Table 1.

To fit volumetric data at excess pressure, linear pressure dependencies were added to eq 28 parameters.

$$\text{PAR} = (a_1 + b_1P) + (a_2 + b_2P)/T + (a_3 + b_3P)T +$$
$$(a_4 + b_4P)/(647 - T) \tag{29}$$

P is the absolute pressure in MPa. When the high-pressure data were introduced, it was found that the pattern was fully consistent for the Simonson−Ryther data and for both sets of Franck data at the higher mole fractions of NaOH. At low mole fraction of NaOH, however, the Eberz−Franck[17] data and the Kerschbaum−Franck[18] data crossed the curves for measurements at saturation pressure. This seems improbable, and undoubtedly arose from the large uncertainty of ϕV values calculated from their densities at low concentrations. Thus, we decided to use the Eberz and the Kerschbaum data only at mole
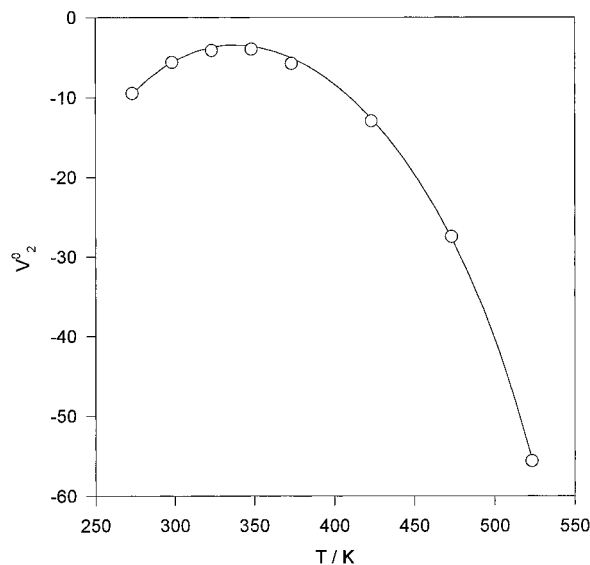
Figure 3. Molar volume V^0_2 at infinite dilution calculated by eq 21. Circles are data points given by Simonson et al.[12]

TABLE 2: Temperature and Pressure Dependencies of Volumetric Parameters

	a_1	a_2	a_3	a_4
$W^V_{1,MX}$	53.386	$-11\,062$	-0.1081	1658
$U^V_{1,MX}$	-28.26	6715	0.0485	0.0
B^V_{MX}	$-10\,618$	$1\,843\,883$	15.22	0.0

|	b_1	b_2	b_3	b_4
$W^V_{1,MX}$	-0.548	106.98	7.83×10^{-4}	-5.75
$U^V_{1,MX}$	1.125	-225.36	-0.0014	0.0
B^V_{MX}	0.0	0.0	0.0	0.0
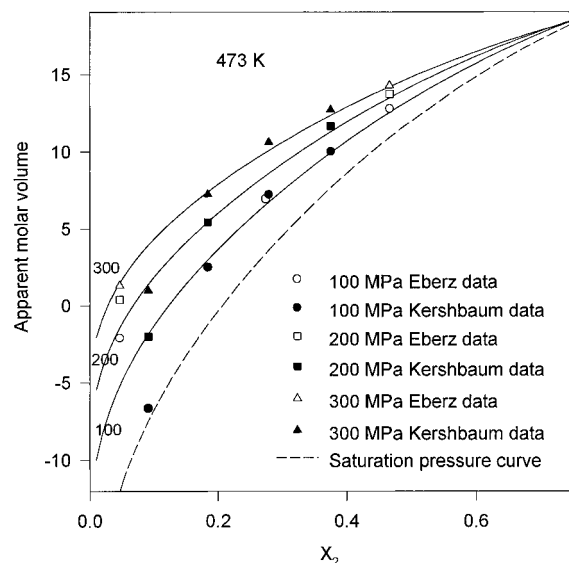
Figure 4. Apparent molar volume at 473 K and different pressures (100, 200, and 300 MPa). Note the increasing deviations at mole fractions below 0.2.

fractions above 0.2 in NaOH along with the Simonson and Ryther data and with the higher weight assigned to the latter.

The resulting parameters are listed in Table 2. The dimensions for U^V, W^V, and B^V are cm³ mol⁻¹ (10^{-6} m³ mol⁻¹), while P is in MPa and T in K. Figures 4 and 5 show some examples of the agreement at particular temperatures.

IV. Activities, Activity Coefficients, Vapor Pressure

The expressions for the activity coefficients were given above in eqs 12 and 13 with the relations to activities in eqs 14 and
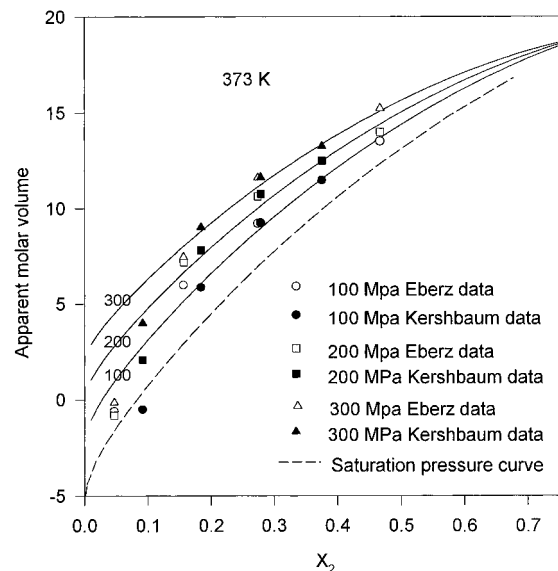
Figure 5. Apparent molar volume at 373 K and different pressures (100, 200, and 300 MPa). Note that the high-pressure data at the mole fractions below 0.2 deviate considerably and even cross the saturation pressure line.

15. Initially the experimental data for 298.15 K were considered. For the high-concentration range there are vapor pressure measurements by Kangro and Groeneveld[24] and by Stokes,[25] as well as isopiestic measurements of Stokes[26] related to the activity values for H_2SO_4(aq) of Shankman and Gordon.[27] In the dilute range there are numerous measurements. Hamer and Wu[28] review all of these references and fit a molality-based equation with a series in powers of the ionic strength in addition to the Debye−Hückel term. This series extends through the sixth power with large coefficients of alternating sign. Clearly, the activity coefficient of aqueous NaOH is surprisingly difficult to represent. For a similar range in molality (0−28 mol kg⁻¹) for aqueous HNO_3, two fewer terms were needed and the higher coefficients are smaller by 2 powers of 10. With the mole fraction based equations, we found that all of the terms in eqs 12 and 13 were needed.

At other temperatures up to 343 K, the electrochemical cell measurements of Akerlof and Kegeles[29] extend to 17 mol kg⁻¹ and are at 10° intervals from 0 to 70 °C. At higher temperatures there are several sources of vapor pressure data.[30−33] Especially important for the present research are those of Dibrov et al.[32] and Krumgalz and Mashovets,[33] which cover a very wide range of composition and extend to 623 K. Also, for compositions up to $x_2 = 0.18$ (6 molal) the activity values of the comprehensive treatment of Simonson et al.[12] were given large weight.

For the higher temperatures the water vapor is not an ideal gas, and a correction of pressure to fugacity must be made. Also, there is a small correction for the difference in overall pressure on the liquid solution from that of pure water. The equation for the activity of water is

$$\ln a_1 = \ln \frac{P}{P^0} - \int_P^{P^0}\left(\frac{V}{RT} - \frac{1}{P}\right)dP + \frac{\bar{V}_1}{RT}(P^0 - P) \quad (30)$$

Again, the initial calculations were made at the saturation pressure of H_2O at each temperature. The temperature dependency adopted previously for parameters $W^V_{1,MX}$, $U^V_{1,MX}$, and B^V_{MX} in eq 28 was found to be satisfactory over the temperature range 273.15−523.15 K. Thus, we adopt for $W_{1,MX}$, $U_{1,MX}$, $V_{1,MX}$, and B_{MX} the form of eq 28. The coefficients $c_1−c_4$ are listed in Table 1, and examples of fit at several temperatures are shown in Figures 6 and 7.
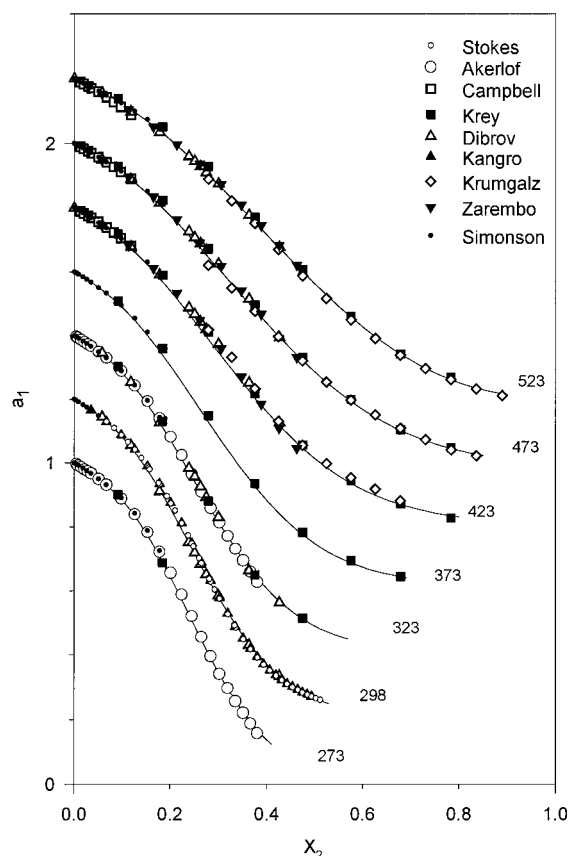
Figure 6. Activity of water at saturation pressure and different temperatures. For convenience of representation, the curves were shifted 0.2 for 298 K, 0.4 for 323 K, and so on.
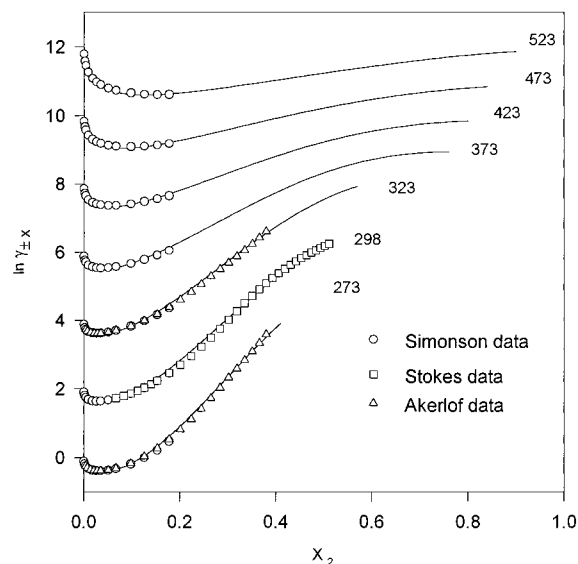
Figure 7. Mean activity coefficient NaOH on a mole fraction basis at saturation pressure and different temperatures. Experimental data at x_2 below 0.18 are from Simonson et al.,[12] those at 298 K are from Stokes,[26] and those at 273 and 323 K are from Akerlof and Kegeles.[29] For convenience of representation, the curves were shifted 2 for 298 K, 4 for 323 K, and so on.

While the variation of saturation pressure up to 523 K is not large, it is desirable to have an expression for the Gibbs energy in a form for convenient differentiation at constant pressure to yield the enthalpy, entropy, and heat capacity. Hence, the activity data were converted to a single reference pressure for the final evaluation of expressions for $W_{1,MX}$, $U_{1,MX}$, $V_{1,MX}$, and B_{MX}.

TABLE 3: Temperature Dependencies of Parameters at Reference Pressure ($P_r = 0$)

	d_1	d_2	d_3	d_4
$W_{1,MX}$	3.026	−2597	0.0	0.0
$U_{1,MX}$	−10.944	5054	0.0	0.0
B_{MX}	104.820	0.0	−0.212	0.0
$V_{1,MX}$	53.211	−15 408	−0.046	0.0

TABLE 4: Water Activities at Saturation Pressure

x_2	273.15	298.15	323.15	373.15	423.15	473.15	523.15
0.00	1.000 0	1.000 0	1.000 0	1.000 0	1.000 0	1.000 0	1.000 0
0.05	0.951 5	0.950 5	0.950 4	0.951 8	0.954 7	0.958 6	0.963 4
0.10	0.883 0	0.881 6	0.882 5	0.888 4	0.897 6	0.908 9	0.922 0
0.15	0.780 7	0.783 7	0.789 5	0.805 9	0.825 8	0.847 7	0.871 4
0.20	0.645 4	0.658 3	0.673 2	0.706 0	0.740 5	0.775 6	0.811 6
0.25	0.493 2	0.518 0	0.543 6	0.595 1	0.645 8	0.695 2	0.744 0
0.30	0.346 8	0.380 7	0.414 7	0.481 9	0.547 1	0.609 7	0.670 6
0.35	0.225 4	0.262 1	0.299 6	0.375 3	0.450 1	0.522 8	0.593 4
0.40	0.136 9	0.170 6	0.206 4	0.282 0	0.359 9	0.437 8	0.514 8
0.45		0.106 7	0.137 2	0.205 6	0.280 3	0.357 9	0.436 9
0.50		0.065 4	0.089 4	0.146 7	0.213 1	0.285 4	0.361 7
0.55			0.058 4	0.103 4	0.158 7	0.221 8	0.291 2
0.60				0.073 0	0.116 2	0.167 7	0.227 0
0.65				0.052 2	0.084 0	0.123 1	0.170 3
0.70				0.038 5	0.060 2	0.087 4	0.122 1
0.75				0.029 7	0.042 8	0.059 6	0.082 7
0.80					0.030 2	0.038 7	0.052 1
0.85						0.023 3	0.029 7
0.90							0.014 4

TABLE 5: ln $\gamma_{\pm,x}$ at Saturation Pressure

x_2	273.15	298.15	323.15	373.15	423.15	473.15	523.15
0.01	−0.337 9	−0.341 1	−0.357 9	−0.419 1	−0.508 5	−0.627 8	−0.789 5
0.02	−0.395 0	−0.389 6	−0.406 6	−0.485 2	−0.606 8	−0.769 7	−0.987 1
0.03	−0.416 3	−0.401 7	−0.417 2	−0.507 6	−0.653 5	−0.849 2	−1.107 8
0.04	−0.417 5	−0.394 4	−0.408 3	−0.508 6	−0.675 3	−0.898 8	−1.191 4
0.05	−0.403 6	−0.373 3	−0.386 2	−0.496 2	−0.681 8	−0.930 2	−1.252 4
0.10	−0.165 4	−0.125 9	−0.150 5	−0.322 1	−0.597 3	−0.950 5	−1.389 3
0.15	0.288 8	0.292 0	0.224 1	−0.042 9	−0.416 0	−0.864 9	−1.397 1
0.20	0.895 2	0.824 4	0.686 6	0.293 1	−0.189 4	−0.733 3	−1.349 2
0.25	1.596 9	1.425 6	1.199 3	0.658 4	0.058 9	−0.579 3	−1.272 7
0.30	2.341 5	2.054 6	1.730 1	1.032 1	0.314 1	−0.415 6	−1.180 9
0.35	3.082 5	2.675 6	2.251 1	1.397 3	0.565 3	−0.250 0	−1.081 2
0.40	3.779 9	3.257 8	2.738 7	1.740 3	0.804 4	−0.088 0	−0.977 8
0.45		3.776 1	3.173 9	2.050 0	1.025 1	0.066 8	−0.873 6
0.50		4.211 7	3.542 3	2.318 3	1.222 7	0.211 6	−0.770 5
0.55			3.833 9	2.539 6	1.394 2	0.344 5	−0.669 8
0.60				2.710 9	1.537 6	0.464 2	−0.572 8
0.65				2.831 9	1.652 2	0.569 6	−0.480 7
0.70				2.905 0	1.738 9	0.660 4	−0.394 7
0.75				2.935 1	1.799 3	0.736 2	−0.316 2
0.80					1.836 4	0.797 0	−0.246 9
0.85						0.843 2	−0.188 6
0.90							−0.143 6

The equations for this recalculation were derived from eqs 12 and 13. For each value of γ_1 or $\gamma_{\pm,x}$, one has

$$\ln \gamma_1(P_r) - \ln \gamma_1(P) = 2[A_x(P_r) - A_x(P)]I_x^{3/2}/(1 + \rho I_x^{1/2}) -$$
$$(x_2^2/4)\exp(-\alpha I_x^{1/2})\int_P^{P_r}(\partial B_{MX}/\partial P)\,dP +$$
$$x_2^2\left[\int_P^{P_r}(\partial W_{1,MX}/\partial P)\,dP + (x_2 - x_1)\int_P^{P_r}(\partial U_{1,MX}/\partial P)\,dP\right] \quad (31)$$

$$\ln \gamma_{\pm,x}(P_r) - \ln \gamma_{\pm,x}(P) = -[A_x(P_r) - A_x(P)][(2/\rho)\ln(1 +$$
$$\rho I_x^{1/2}) + I_x^{1/2}(1 - 2I_x)/(1 + \rho I_x^{1/2})] + (x_2/4)\,[g(\alpha I_x^{1/2}) +$$
$$(1 - x_2)\exp(-\alpha I_x^{1/2})]\int_P^{P_r}(\partial B_{MX}/\partial P)\,dP + (x_1^2 -$$
$$1)\int_P^{P_r}(\partial W_{1,MX}/\partial P)\,dP + 2(x_1^2 x_2)\int_P^{P_r}(\partial U_{1,MX}/\partial P)\,dP \quad (32)$$

where P and P_r are saturation and reference pressures respectively.

TABLE 6: ln $\gamma_{\pm,m}$ at Saturation Pressure

					T/K			
m	x_2	273.15	298.15	323.15	373.15	423.15	473.15	523.15
5	0.153	0.1520	0.1521	0.0812	−0.1919	−0.5705	−1.0245	−1.5613
6	0.178	0.4147	0.3807	0.2768	−0.0572	−0.4897	−0.9914	−1.5709
7	0.201	0.6891	0.6158	0.4757	0.0782	−0.4075	−0.9541	−1.5723
8	0.224	0.9667	0.8508	0.6727	0.2111	−0.3264	−0.9153	−1.5687
9	0.245	1.2413	1.0811	0.8646	0.3393	−0.2479	−0.8766	−1.5623
10	0.265	1.5085	1.3038	1.0490	0.4618	−0.1730	−0.8389	−1.5543
12	0.302	2.0101	1.7187	1.3905	0.6866	−0.0358	−0.7687	−1.5366
14	0.335	2.4591	2.0874	1.6920	0.8833	0.0840	−0.7069	−1.5194
16	0.366	2.8524	2.4085	1.9534	1.0527	0.1868	−0.6538	−1.5042
18	0.393	3.1918	2.6843	2.1772	1.1969	0.2740	−0.6089	−1.4914
20	0.419	3.4814	2.9188	2.3668	1.3186	0.3472	−0.5714	−1.4812
22	0.442	3.7261	3.1164	2.5262	1.4205	0.4083	−0.5405	−1.4736
24	0.464	3.9314	3.2816	2.6591	1.5051	0.4587	−0.5155	−1.4682

Values of $(\partial W_{1,MX}/\partial P)_T$, $(\partial U_{1,MX}/\partial P)_T$ and $(\partial B_{MX}/\partial P)$ dP were derived from the volumetric fit according to eqs 24−26. $V_{1,MX}^V$ was not used for the volumetric fit. Since $W_{1,MX}^V$, $U_{1,MX}^V$, and B_{MX}^V were expressed in the form of eq 29, the final expressions for recalculation of activities of solute and solvent to a reference pressure P_r are

$$\ln \gamma_1(P_r) - \ln \gamma_1(P) = 2[A_x(P_r) - A_x(P)]I_x^{3/2}/(1 + \rho I_x^{1/2}) -$$
$$(x_2^2/4RT) \exp(-\alpha I_x^{1/2}) (a_1^B + a_2^B/T + a_3^B T)(P_r - P) +$$
$$x_2^2/RT\{(a_1^W P_r + b_1^W P_r^2/2) - (a_1^W P + b_1^W P^2/2) +$$
$$[(a_2^W P_r + b_2^W P_r^2/2) - (a_2^W P + b_2^W P^2/2)]/T + [(a_3^W P_r +$$
$$b_3^W P_r^2/2) - (a_3^W P + b_3^W P^2/2)] T + [(a_4^W P_r + b_4^W P_r^2/2) -$$
$$(a_4^W P + b_4^W P^2/2)]/(647 - T)\} + x_2^2(x_2 - x_1)/RT\{(a_1^U P_r +$$
$$b_1^U P_r^2/2) - (a_1^U P + b_1^U P^2/2) + [(a_2^U P_r + b_2^U P_r^2/2) -$$
$$(a_2^U P + b_2^U P^2/2)]/T + [(a_3^U P_r + b_3^U P_r^2/2) - (a_3^U P +$$
$$b_3^U P^2/2)] T\} \quad (33)$$

$$\ln \gamma_{\pm,x}(P_r) - \ln \gamma_{\pm,x}(P) = -[A_x(P_r) - A_x(P)][(2/\rho) \ln(1 +$$
$$\rho I_x^{1/2}) + I_x^{1/2}(1 - 2I_x)/(1 + \rho I_x^{1/2})] + (x_2/4RT) [g(\alpha I_x^{1/2}) +$$
$$(1 - x_2) \exp(-\alpha I_x^{1/2})] (a_1^B + a_2^B/T + a_3^B T)(P_r - P) +$$
$$[(x_1^2 - 1)/RT] \{(a_1^W P_r + b_1^W P_r^2/2) - (a_1^W P + b_1^W P^2/2) +$$
$$[(a_2^W P_r + b_2^W P_r^2/2) - (a_2^W P + b_2^W P^2/2)]/T + [(a_3^W P_r +$$
$$b_3^W P_r^2/2) - (a_3^W P + b_3^W P^2/2)] T + [(a_4^W P_r + b_4^W P_r^2/2) -$$
$$(a_4^W P + b_4^W P^2/2)]/(647 - T)\} + (2x_1^2 x_2/RT)\{(a_1^U P_r +$$
$$b_1^U P_r^2/2) - (a_1^U P + b_1^U P^2/2) + [(a_2^U P_r + b_2^U P_r^2/2) -$$
$$(a_2^U P + b_2^U P^2/2)]/T + [(a_3^U P_r + b_3^U P_r^2/2) - (a_3^U P +$$
$$b_3^U P^2/2)] T\} \quad (34)$$

In eqs 33 and 34, the superscripts B, W, U indicate volumetric parameters from Table 2.

The entire set of data at the reference pressure was then fitted, and coefficients were obtained. Calculations were made both for $P_r = 0$ and $P_r = 20$ MPa. The same temperature dependency was assumed as that of eq 28 for the volumetric parameters

$$\text{PAR}_{P_r} = d_1 + d_2/T + d_3 T + d_4/(647 - T) \quad (35)$$

Good fits were obtained for either reference pressure. The resulting parameters for $P_r = 0$ are given in Table 3.

The parameters in Table 3 are for zero pressure and are valid for one bar (0.1 MPa) or any small pressure. Each of the

volumetric parameters , B_{MX}^V, $W_{1,MX}^V$, $U_{1,MX}^V$, and $V_{1,MX}^V$ is defined as RT times the pressure derivative of the parent (Gibbs energy) parameter B_{MX}, $W_{1,MX}$, $U_{1,MX}$ (eqs 12−14). Thus, we have pressure-dependent expressions for each parameter d_1, d_2, and d_3.

$$d_i(P) = d_i(P = 0) + (a_i P + b_i P^2/2)/RT \quad (36)$$

Note that an additional temperature dependency is introduced for the pressure-dependent terms.

In view of the various sources of experimental data and the uncertainties as to their accuracy, it is impractical to give precise uncertainties for the derived parameters. All values in Tables 1, 2, and 3 are rounded so that the estimated uncertainty is in the final digit.

Values of the activity of water, a_1, and the activity coefficient of NaOH, $\gamma_{\pm,x}$, at even temperatures and mole-fractions are given in Tables 4 and 5. For convenience in some applications, the activity coefficients for NaOH were converted to a molality basis; values for 5−25 mol kg^{-1} are given in Table 6. For smaller molalities the values of Simonson et al.[12] should be used.

V. Discussion

The advantages of the present form of the equation include (1) representation in simple form of data to very high concentration or to pure liquid electrolyte, and (2) convenient and rigorous extension to mixed electrolytes with any number of components.[3−8]

The present results will provide the NaOH−H$_2$O parameters not only for the binary but also for more complex mixtures. A similar but less extensive and complex study for KOH−H$_2$O was recently completed in this laboratory.[11] In the future, calculations will be extended to the solubility limits for various mixed systems.

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