Comprehensive Model of Synthetic Bayer Liquors. Part 2. Densities of Alkaline Aluminate Solutions to 90 °C

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Densities of $NaOH + NaAl(OH)_4$ solutions were measured in isomolal series at ionic strengths (I) over the range of $1 \leq I/\text{mol kg}^{-1} \leq 6$ and at total concentration ratios of $0 \leq [Al(III)]_T/[Na^+]_T \leq 0.6$ in the temperature range of $50 \leq t/°C \leq 90$. A Pitzer model representing the volumetric properties of hypothetical pure sodium aluminate solutions was derived and incorporated into our thermodynamic model of synthetic Bayer liquor solutions consisting of the components $NaOH + NaAl(OH)_4 + Na_2CO_3 + Na_2SO_4 + NaCl + NaF + Na_2C_2O_4$ (sodium oxalate) + $NaHCOO$ (sodium formate) + $NaCH_3COO$ (sodium acetate) + H_2O. The model calculations agree with experimental densities of twelve 7-component synthetic Bayer liquors to better than 0.1%.

Introduction

In thermodynamically consistent electrolyte models, volumetric properties of the components (solution densities) are required to calculate the variation of other thermodynamic quantities as a function of pressure. Furthermore, density is needed for the interconversion of concentration units and is an important process parameter in the industrial context because it is required for engineering design purposes related to sizing and various heat- and mass-transfer operations. The present paper is part of a series on the thermodynamic properties of synthetic Bayer liquors. It deals with the experimental determination and modeling of the densities of alkaline sodium aluminate solutions at superambient temperatures. As a continuation of previous measurements at 25 °C,[1] mixtures were measured at (50, 70, and 90) °C in isomolal series at $1 \leq I/\text{mol kg}^{-1} \leq 6$ with $0 \leq [Al(III)]_T/[Na^+]_T \leq 0.6$ using a commercially available Hastelloy vibrating tube densimeter. The data so obtained have been incorporated into our 10-component synthetic Bayer liquor Pitzer model, which aims at improved modeling capabilities for predicting the thermodynamic properties of Bayer process solutions employed in alumina production.[2]

Despite (or perhaps because of) their industrial importance, only very few studies have been published in the open literature that report experimental density data of alkaline sodium aluminate solutions over wider temperature and concentration ranges.[3−7] The present work covers conditions that are relevant to the gibbsite precipitation stage of the Bayer process.

Density Measurements at High Temperature

Equipment. Previous density measurements on alkaline aluminate solutions at 25 °C[1] were made using a vibrating glass tube densimeter. At higher temperatures, caustic solutions containing either CO_3^{2-} or OH^- proved to be too corrosive toward the glass tube, preventing accurate density determinations. To resolve this problem, we employed an Anton Paar DMA 512 P densimeter with a vibrating tube constructed from Hastelloy C276 in this work.

To facilitate the protection of the samples from atmospheric CO_2 and their transfer into the densimeter, we developed an appropriate injection system. This comprised a narrow-diameter (ca. 3 mm) high-quality stainless steel tubing fitted with stainless steel Swagelok valves and Luer lock joints at the entry and exit points.

Temperature control was maintained with a Julabo F-33 thermostat-circulator. The temperature was monitored continuously using precision thermistors calibrated against a quartz crystal thermometer (Hewlett-Packard, model HP 2804A) that had been calibrated against the triple point of water with an overall accuracy of ±0.02 °C. Temperatures were found to be (50.00 ± 0.02) °C, (70.00 ± 0.02) °C, and (90.00 ± 0.03) °C over the entire period of the measurement.

Density measurements for a given sample with vibrating tube densimeters typically involve at least three measurements. For a vibrating tube at constant temperature and pressure, the square of the oscillation period of the tube depends on the density of the fluid contained within it. The density of the solution, ρ_s, was calculated according to

$$\rho_s - \rho_w = k(\tau_s^{\,2} - \tau_w^{\,2}) \tag{1}$$

where τ_s and τ_w represent the periods of oscillation of the densimeter tube containing the solution and pure water, respectively, and ρ_w represents the density of water at the conditions at which the measurement is made.

The densimeter constant k was determined by the measurement of τ^2 for standard materials of accurately known density. Water and air (or nitrogen) are generally used for this purpose.

$$k = \frac{\rho_w - \rho_{air}}{\tau_w^{\,2} - \tau_{air}^{\,2}} \tag{2}$$

The density data used for the calibration of the densimeter are presented in Table 1. The densities of air were calculated from the equation given for dry air in the Rubber Handbook.[8] The densities of water are essentially identical to those derived from the NIST/ASME database[9] and the

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Table 1. Densities of Dry Air and Water as Used in This Study

t/°C	ρ_{air}/g·cm^{-3}	ρ_{water}/g·cm^{-3}
25	0.001185	0.997043
50	0.001093	0.988030
70	0.001030	0.977759
90	0.000973	0.965303

IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam.[10]

Method Development. Static density measurements at superambient temperatures require careful attention to the experimental protocol. Accordingly, the following procedure was developed using NaCl(aq) solutions whose densities are accurately known as a function of temperature and concentration.[11]

After samples were introduced into the densimeter using a polyethylene syringe, the two Swagelok valves were closed, and the sample was equilibrated for 10 min with continuous monitoring of the tube temperature. During this time, the thermal expansion of the sample caused a small buildup of pressure within the vibrating tube. Although the DMA 512 P is able to operate at high pressures, this small increase in pressure detectably affects the density. To reduce the pressure in the densimeter sample to that of the atmosphere, we opened the upper valve briefly. (To avoid outgassing of dissolved air at this point and consequent instability of the reading, it is essential to use degassed solutions.) This typically resulted in a slight decrease in the oscillation period, which stabilized after ca. 3 min. Subsequent brief openings of the upper valve saw no change in the oscillation period, and this value was then taken as the equilibrium reading at (constant) atmospheric pressure. At higher temperatures, longer and more numerous re-equilibration periods were required. Air typically required only one release of pressure and took less time to attain stability, suggesting that the (small) changes in the oscillation period for liquids were probably related to their higher viscosity (cf. air) and perhaps slight outgassing.

Validation. The experimental protocol was tested using NaCl solutions at notional concentrations of (1, 2, and 3) mol kg^{-1}. Solutions were prepared from dried NaCl (BDH Analar, >99.5%) and freshly degassed water with appropriate buoyancy corrections. Final degassing of the solutions was achieved by applying vacuum to the sample in the injecting syringe immediately prior to injection into the densimeter. This method, which has been employed successfully elsewhere,[12] generated results in good agreement with literature values (Figure 1).

Measurement of NaOH/NaAl(OH)$_4$ Mixtures. In principle, the above method is valid for NaOH/NaAl(OH)$_4$ mixtures that were prepared as described previously.[15] However, the Hastelloy C276 vibrating tube was found to require a degree of preconditioning before reproducible oscillation periods could be attained with these chemically aggressive solutions. Thus, samples were introduced into the densimeter and equilibrated for (10 to 30) min prior to measurement. At higher ionic strengths, the final (in-syringe) degassing procedure became problematic because gas bubbles failed to evolve adequately because of the greatly increased viscosity. Because of this, the in-syringe degassing of the solution prior to injection was omitted with some loss of experimental efficiency. Stable readings were obtained following suitable conditioning periods.

In contrast to the measurements at lower temperatures, considerable difficulties were experienced in obtaining satisfactory densities at 90 °C. In part this was due to a malfunction in the densimeter seals. However, following replacement of the seals, problems were still encountered with reproducibility. Even after repeated injections the vibration periods continued to increase (corresponding to an apparent increase in density), which could possibly be explained by a slow reaction between the hot alkaline aluminate solutions and the Hastelloy vibrating tube of the densimeter or by microprecipitation of gibbsite in the tube. Subsequent flushing with NaOH followed by measurement of the water period resulted in stable and reproducible values of the vibration period for water. This appears, at least at first sight, to be consistent with precipitation. However, repeat measurements with NaOH(aq) at 90 °C also showed this variability. Thus, some (uncharacterized) problem with the performance of the densimeter cannot be ruled out. These difficulties have been reflected in the data by restricting their listing to five decimal places rather than the usual six. It must be understood, however, that the real uncertainties are likely to be considerably higher (ca. 10^{-3} g cm^{-3} at 90 °C as compared to 10^{-4} g cm^{-3} at 50 °C and 70 °C).

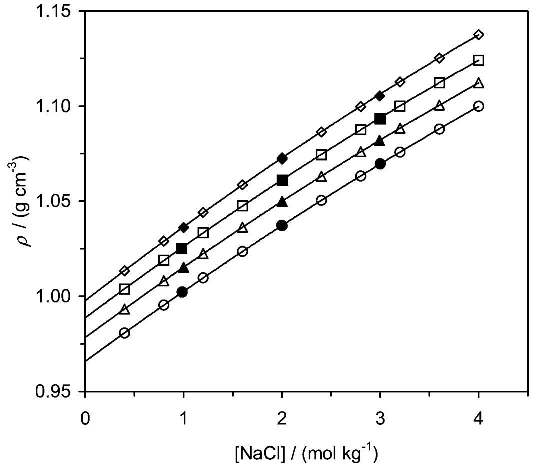

Figure 1. NaCl densities measured by the Hastelloy DMA 512 P densimeter (solid symbols). From top to bottom, t/°C = 25, 50, 70, and 90. Open symbols are averaged literature data taken from the JESS database.[13,14] Solid lines were calculated from a volumetric Pitzer model for NaCl(aq).[11]

Densities of NaOH/NaAl(OH)$_4$ Mixtures

The results of the density measurements at 50 °C, 70 °C, and 90 °C are presented in Tables 2, 3, and 4, respectively. Composition is expressed in terms of molality (mol of solute/kg of solvent). Note that [NaOH]$_T$ is here defined as the sum of the total stoichiometric free NaOH plus the aluminate molality.

$$[\mathrm{NaOH}]_{\mathrm{T}} = [\mathrm{NaOH}]_{\mathrm{free}} + [\mathrm{Al(III)}]_{\mathrm{T}} \qquad (3)$$

For convenience, the data have also been converted into two industrial units: C (concentration of NaOH expressed as g of Na$_2$CO$_3$/L of solution) and A/C (the aluminum to caustic ratio—the ratio between the masses of aluminum expressed as g of Al$_2$O$_3$/L and NaOH expressed as g of Na$_2$CO$_3$/L). Buoyancy corrections were used throughout.

The densities obtained are plotted in Figures 2, 3, and 4 for 50 °C, 70 °C, and 90 °C, respectively. The densities of NaOH/NaAl(OH)$_4$ mixtures display essentially linear trends ($0.0001 < \sigma < 0.001$ for 50 °C and 70 °C, $0.0001 < \sigma < 0.0036$ for 90 °C) with respect to increasing Al(OH)$_4^-$ substitution at constant I, similar to those at 25 °C.[1] This linearity (dashed lines) allows an estimation of the densi-

Table 2. Densities ρ of Aqueous NaOH + $NaAl(OH)_4$ Mixtures at Constant Molality at t = 50 °C

$[NaOH]_T$/mol·kg^{-1}	$[Al(III)]_T$/mol·kg^{-1}	C^a/g·L^{-1}	A/C^b	ρ/g·cm^{-3}
	I = 1 mol·kg^{-1}			
1.0004	0	52.50	0	1.029846
0.9982	0.1008	52.10	0.097	1.031956
1.0022	0.2000	52.06	0.192	1.034846
0.9989	0.3000	51.66	0.289	1.037691
0.9995	0.3995	51.46	0.385	1.040541
0.9978^d	0.3998	51.37	0.385	1.040490
1.0004	0.5001	51.27	0.481	1.043441
0.9989	0.5999	50.96	0.578	1.046210
1.00	1.00			1.05720^c
	I = 2 mol·kg^{-1}			
2.0057	0	105.11	0	1.068184
1.9993	0.2002	103.70	0.096	1.072281
2.0011	0.4002	102.84	0.192	1.077628
2.0005	0.5999	101.88	0.288	1.082900
1.9976	0.7998	100.83	0.385	1.088034
1.9991^d	0.8000	100.93	0.385	1.088341
1.9978	0.9998	99.95	0.481	1.093111
1.9994	1.1996	99.12	0.577	1.097816
2.00	2.00			1.11822^c
	I = 3 mol·kg^{-1}			
3.0037	0	156.83	0	1.103607
3.0044	0.3002	154.54	0.096	1.110027
3.0026	0.5996	152.37	0.192	1.117325
2.9988^d	0.5998	152.25	0.192	1.117747
3.0009	0.8998	150.20	0.288	1.124133
3.0000	1.1992	148.24	0.385	1.131544
2.9995	1.4996	146.28	0.481	1.138297
2.9997	1.7994	144.44	0.577	1.145194
3.00	3.00			1.17316^c
	I = 4 mol·kg^{-1}			
4.0040	0	207.92	0	1.136818
4.0041	0.4000	203.97	0.096	1.145150
3.9969^d	0.3997	203.62	0.096	1.144985
4.0036	0.7998	200.32	0.192	1.154237
4.0004	1.1997	196.70	0.288	1.163126
3.9977	1.5991	193.17	0.385	1.171340
3.9996	1.9996	190.00	0.481	1.179612
4.0019	2.3991	186.97	0.577	1.187697
4.00	4.00			1.22242^c
	I = 5 mol·kg^{-1}			
5.0064	0	258.18	0	1.167970
4.9994	0.4995	251.13	0.096	1.179000
5.0013	0.9994	246.48	0.192	1.188508
5.0005	1.4995	241.20	0.288	1.198693
4.9998	1.9996	236.12	0.385	1.208336
4.9994	2.4994	231.32	0.481	1.217925
4.9970	2.9997	226.63	0.577	1.227117
4.9971^d	2.9995	226.60	0.577	1.226927
5.00	5.00			1.26650^c
	I = 6 mol·kg^{-1}			
6.0076	0	307.28	0	1.197102
5.9994	0.5996	298.62	0.096	1.208556
6.0017	1.1998	291.05	0.192	1.220398
5.9996	1.7997	283.70	0.289	1.231666
6.0006	2.3994	276.82	0.385	1.242349
5.9981	2.9995	270.17	0.481	1.252753
5.9983	3.5997	263.91	0.577	1.262522
6.00	6.00			1.30740^c

[a] Concentration of Na^+ expressed in terms of g of Na_2CO_3/L of solution. [b] Mass ratio of total Al(III) (expressed as g of Al_2O_3) to total Na^+ (expressed as g of Na_2CO_3). [c] Values for the hypothetical pure $NaAl(OH)_4$ electrolyte solutions, obtained by linear extrapolation to 100% substitution of OH^- with $Al(OH)_4{}^-$. [d] Independent duplication.

Table 3. Densities ρ of Aqueous NaOH + $NaAl(OH)_4$ Mixtures at Constant Molality at t = 70 °C

$[NaOH]_T$/mol·kg^{-1}	$[Al(III)]_T$/mol·kg^{-1}	C^a/g·L^{-1}	A/C^b	ρ/g·cm^{-3}
	I = 1 mol·kg^{-1}			
0.9990	0	51.82	0	1.017893
0.9999	0.0999	51.63	0.096	1.020889
0.9976	0.2000	51.28	0.193	1.023800
0.9987	0.2998	51.10	0.289	1.026676
1.0000	0.3998	50.95	0.385	1.029755
1.0000	0.4995	50.71	0.481	1.032450
0.9984	0.5999	50.40	0.578	1.035271
1.00	1.00			1.04697^c
	I = 2 mol·kg^{-1}			
2.0007	0	103.61	0	1.055415
1.9987	0.2002	102.56	0.096	1.060780
1.9986	0.4001	101.65	0.193	1.066388
1.9995^d	0.4001	101.67	0.192	1.066218
1.9977	0.5997	100.69	0.289	1.071550
1.9978	0.7985	99.80	0.384	1.076684
1.9993	1.0000	99.00	0.481	1.081992
1.9989	1.1996	98.12	0.577	1.087021
2.00	2.00			1.10828^c
	I = 3 mol·kg^{-1}			
3.0017	0	154.96	0	1.091106
3.0008	0.3000	152.73	0.096	1.098188
2.9988	0.5995	150.59	0.192	1.105551
3.0000	0.8996	148.63	0.288	1.112689
2.9999	1.1996	146.71	0.385	1.119940
2.9985	1.4994	144.79	0.481	1.127027
2.9997^d	1.4995	144.83	0.481	1.126937
2.9987	1.7994	142.95	0.577	1.133682
2.9985^d	1.7993	142.90	0.577	1.133358
3.00	3.00			1.16223^c
	I = 4 mol·kg^{-1}			
3.9984	0	205.26	0	1.123631
3.9996	0.3999	201.59	0.096	1.132893
4.0008	0.7999	198.04	0.192	1.141830
3.9994	1.1996	194.55	0.289	1.150680
3.9989	1.5998	191.25	0.385	1.159418
3.9988	1.9995	188.09	0.481	1.167949
3.9982	2.3993	185.12	0.577	1.176927
4.00	4.00			1.21236^c
	I = 5 mol·kg^{-1}			
4.9973	0	254.82	0	1.154537
4.9977	0.4999	249.12	0.096	1.165286
5.0005	0.9996	243.86	0.192	1.176029
4.9983	1.4999	238.58	0.289	1.186138
4.9985^d	1.4995	238.51	0.289	1.185760
4.9986	1.9995	233.67	0.385	1.196054
4.9999	2.4996	228.94	0.481	1.205295
5.0001	2.9996	224.44	0.577	1.214594
5.00	5.00			1.25553^c
	I = 6 mol·kg^{-1}			
6.0039	0	303.78	0	1.184029
5.9969	0.5999	295.24	0.096	1.195322
5.9968	1.2000	287.74	0.192	1.207362
6.0018	1.7993	280.91	0.288	1.219183
5.9988	2.3995	273.91	0.385	1.229641
6.0003	2.9988	267.50	0.481	1.239940
5.9974	3.5996	261.20	0.577	1.249753
6.00	6.00			1.29506^c

[a] Concentration of Na^+ expressed in terms of g of Na_2CO_3/L of solution. [b] Mass ratio of total Al(III) (expressed as g of Al_2O_3) to total Na^+ (expressed as g of Na_2CO_3). [c] Values for the hypothetical pure $NaAl(OH)_4$ electrolyte solutions, obtained by linear extrapolation to 100% substitution of OH^- with $Al(OH)_4{}^-$. [d] Independent duplication.

ties of the hypothetical pure $NaAl(OH)_4$ end-member solution through extrapolation of the mixture densities. Actually, a close inspection of the present data reveals a very slight convex curvature, particularly at higher ionic strengths. This is consistent with Miller's analysis,[16] which showed that a Young's rule (linear) dependency of density on composition in mixtures is, strictly speaking, realized only on volume-based concentration scales, although the deviations for mass-based concentration scales are small. The volumetric Pitzer model developed in this work (see below) reproduces this very slight convex curvature accurately (solid lines).

Table 4. Densities ρ of Aqueous NaOH + NaAl(OH)$_4$ Mixtures at Constant Molality at t = 90 °C

[NaOH]$_T$/mol·kg^{-1}	[Al(III)]$_T$/mol·kg^{-1}	C[a]/g·L^{-1}	A/C[b]	ρ/g·cm^{-3}
	I = 1 mol·kg^{-1}			
1.0024	0	51.36	0	1.00562
1.0000	0.1000	51.01	0.096	1.00847
1.0000	0.2000	50.78	0.192	1.01148
0.9994	0.2999	50.52	0.289	1.01439
1.0007	0.3999	50.35	0.384	1.01710
0.9992	0.4997	50.06	0.481	1.01993
1.0004	0.5997	49.89	0.577	1.02277
1.00	1.00			1.0343[c]
	I = 2 mol·kg^{-1}			
2.0008	0	102.38	0	1.04280
2.0006	0.4004	100.53	0.193	1.05366
2.0004	0.7996	98.29	0.385	1.05923
2.0000[d]	0.8003	98.72	0.385	1.06406
1.9992	1.1996	96.40	0.577	1.06776
2.00	2.00			1.0860[c]
	I = 3 mol·kg^{-1}			
3.0065	0.0000	153.35	0.000	1.07824
2.9992	0.8999	146.48	0.289	1.09315
3.0000	1.1997	144.58	0.385	1.10125
3.00	3.00			1.1336[c]
	I = 4 mol·kg^{-1}			
4.0015	0	203.08	0	1.11095
3.9991	0.3998	198.87	0.096	1.11774
3.9989	0.7998	195.38	0.192	1.12695
3.9993	1.1997	192.22	0.289	1.13689
3.9987	1.5996	189.09	0.385	1.14638
4.0000	1.9994	185.93	0.481	1.15425
3.9995	2.3994	182.80	0.577	1.16186
4.00	4.00			1.1977[c]
	I = 5 mol·kg^{-1}			
4.9980	0	251.97	0	1.14149
4.9992	0.4999	245.82	0.096	1.14960
4.9977	0.9997	240.88	0.192	1.16224
5.0010	1.4996	235.34	0.288	1.16947
4.9989	1.9994	231.03	0.385	1.18250
4.9984[d]	1.9996	231.03	0.385	1.18258
5.0005	2.4992	225.57	0.481	1.18743
4.9995	2.9993	221.25	0.577	1.19746
5.00	5.00			1.2370[c]
	I = 6 mol·kg^{-1}			
5.9996	0	300.13	0	1.17050

[a] Concentration of Na$^+$ expressed in terms of g of Na$_2$CO$_3$/L of solution. [b] Mass ratio of total Al(III) (expressed as g of Al$_2$O$_3$) to total Na$^+$ (expressed as g of Na$_2$CO$_3$). [c] Values for the hypothetical pure NaAl(OH)$_4$ electrolyte solutions, obtained by linear extrapolation to 100% substitution of OH$^-$ with Al(OH)$_4$$^-$. [d] Independent duplication.

The present results indicate that, for most purposes, the densities of these mixtures indeed follow Young's rule behavior on the molality scale to a sufficient level of accuracy. In other words, for the calculation of densities, alkaline sodium aluminate solutions can, at constant ionic strength, be considered to be ideal mixtures of NaOH(aq) and the hypothetical NaAl(OH)$_4$(aq). For such calculations, the linearly extrapolated density values for pure NaAl(OH)$_4$(aq) given in Tables 2 to 4 should be used. Because of its slight curvature, the Pitzer model extrapolates to slightly different density values for NaAl(OH)$_4$(aq).

The experimental difficulties at 90 °C referred to above are readily apparent (Figure 4). Because measurements at I/(mol kg^{-1}) = 2 and 3 were particularly problematic, some of the data for these ionic strengths are not reported numerically but are shown graphically (open symbols). Despite these problems, the densities of the alkaline aluminate solutions at 90 °C are consistent with those obtained at lower temperatures: they are very close to linear functions of the (mole) percentage substitution of OH$^-$ by Al(OH)$_4$$^-$, and the slopes of the curves increase systematically with increasing I.

Densities typically decrease with increasing temperature by virtue of the expansion of the solvent, and this trend is

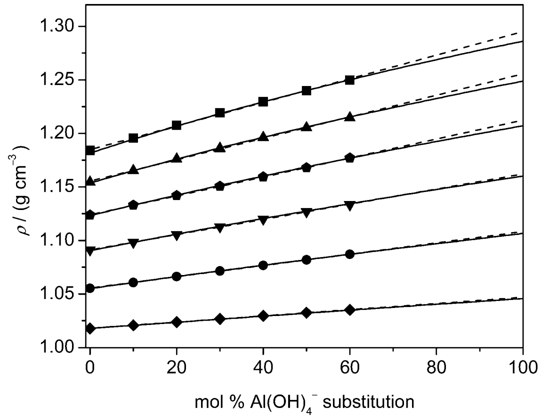

Figure 2. Densities of isomolal series of NaOH/NaAl(OH)$_4$ mixtures at various ionic strengths at 50 °C. From bottom to top, I/(mol kg^{-1}) = 1, 2, 3, 4, 5, and 6. Solid lines, present Pitzer model; dashed lines, linear regression.

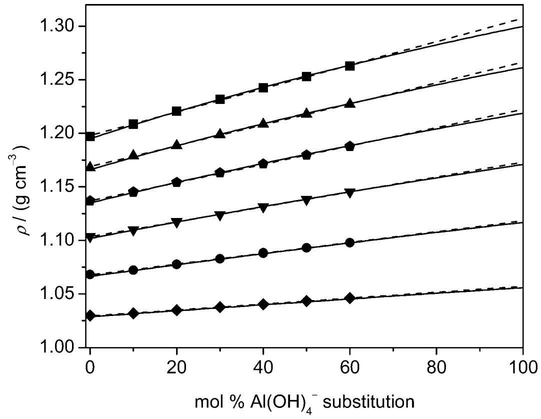

Figure 3. Densities of isomolal series of NaOH/NaAl(OH)$_4$ mixtures at various ionic strengths at 70 °C. From bottom to top, I/(mol kg^{-1}) = 1, 2, 3, 4, 5, and 6. Solid lines, present Pitzer model; dashed lines, linear regression.

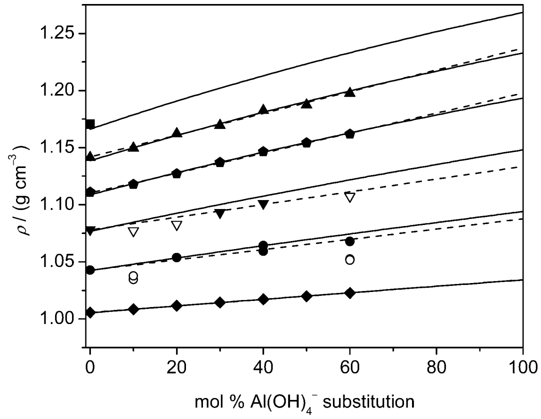

Figure 4. Densities of isomolal series of NaOH/NaAl(OH)$_4$ mixtures at various ionic strengths at 90 °C. From bottom to top, I/(mol kg^{-1}) = 1, 2, 3, 4, 5, and 6. Solid lines, present Pitzer model; dashed lines, linear regression of data represented by solid symbols. The experimental difficulties discussed in the text are obvious from some of the data (open symbols).

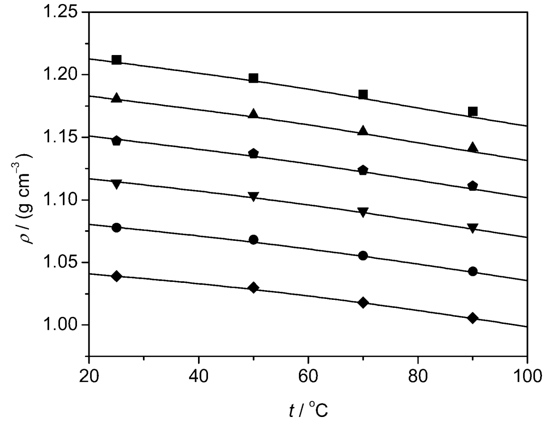

Figure 5. Temperature dependence of NaOH(aq) densities at various ionic strengths. From bottom to top, I/(mol kg^{-1}) = 1, 2, 3, 4, 5, and 6. Data at 25 °C were taken from Sipos et al.[1] Solid lines, present Pitzer model.

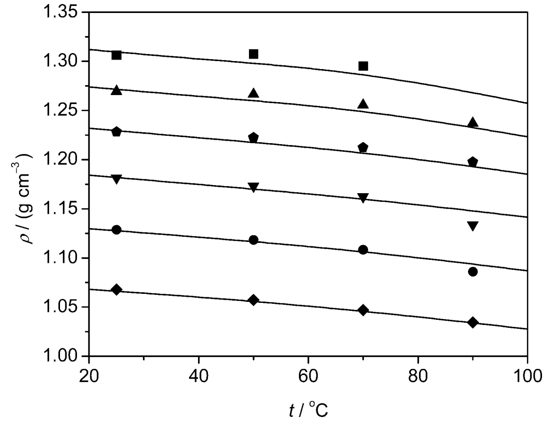

Figure 6. Temperature dependence of hypothetical NaAl(OH)$_4$(aq) densities, obtained by linear extrapolation, at various ionic strengths. From bottom to top, I/(mol kg^{-1}) = 1, 2, 3, 4, 5, and 6. Data at 25 °C were taken from Sipos et al.[1] Solid lines, present Pitzer model.

observed throughout the series of measurements. This effect is illustrated in Figures 5 and 6, in which the densities of the end members at each ionic strength are plotted as a function of temperature. The plots appear to be slightly curved, suggesting that the expansivity of the solutions is slightly temperature-dependent. The Pitzer model employed in this work (see below) reproduces this slight curvature very well. The slopes of the density–temperature plots (i.e., the expansivities) of the NaOH solutions are systematically greater than those of NaAl(OH)$_4$.

The differences between the densities of the end-member solutions are highlighted when expressed as a function of concentration (Figures 7 and 8). These differences may be explained by the difference in electrostrictive interactions between OH$^-$ and Al(OH)$_4^-$ and/or a difference in solvent structure within the solutions.

Volumetric Pitzer Model of NaOH/NaAl(OH)$_4$ Mixtures

Pitzer equations for volumetric properties of electrolyte solutions are given by eq 19 to 23 of part 1 of this series. A temperature function (eq 4 below) for the standard partial molar volume, $V°$, of sodium aluminate was derived from data given for 10 °C to 55 °C by Hovey et al.,[17] obtained by them from a Pitzer/Young's rule analysis of their experimental data together with a value for 200 °C estimated according to the model of Pokrovskii and Helgeson.[18]

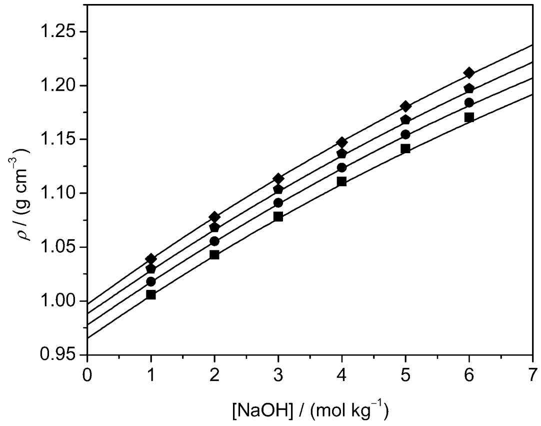

Figure 7. Densities of NaOH(aq) as a function of molality. From top to bottom, t/°C = 25, 50, 70, and 90. Symbols, experimental values; solid lines, present Pitzer model.

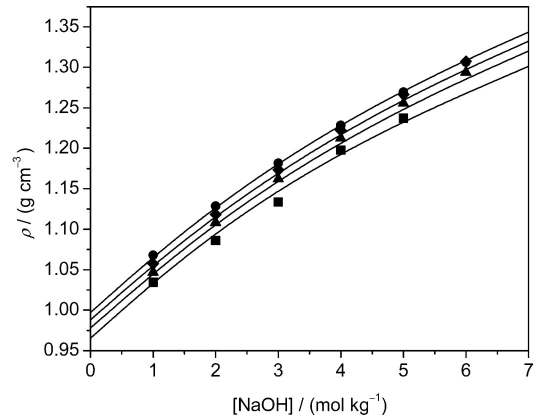

Figure 8. Densities of hypothetical pure NaAl(OH)$_4$(aq), obtained by linear extrapolation, as a function of molality. From top to bottom, t/°C = 25, 50, 70, and 90. Symbols, experimental values; solid lines, present Pitzer model.

$$V°/\mathrm{cm^3\ mol^{-1}} = -7.5427 + 0.357765143T/\mathrm{K} - 0.00056047206(T/\mathrm{K})^2 - \frac{148.47227}{T/\mathrm{K} - 263} \qquad (4)$$

Attempts to base a volumetric model for sodium aluminate on this standard partial molar volume function and on the volumetric Pitzer parameters for NaOH(aq)[19,20] did not adequately reproduce the densities of NaOH/NaAl(OH)$_4$ mixtures. Because the slopes of the lines in Figures 2 to 4 increase systematically with increasing I, the apparent molar volumes of NaOH and NaAl(OH)$_4$ have different concentration dependencies that can be modeled only by different sets of volumetric Pitzer parameters.

The model has therefore been improved by deriving temperature-dependent volumetric Pitzer parameters for NaAl(OH)$_4$ from the present experimental density data (25 ≤ t/°C ≤ 90) reported in this and in our previous[1] work. Densities measured[4,5] at 25 ≤ t/°C ≤ 90 for the ionic strength range of about (4 to 10) mol kg^{-1} and A/C ratios of up to 0.58 were also included but with a lower weight because the reported reproducibilities were about (1 to 4) × 10^{-4} g cm^{-3} or less. The optimization was performed with the ChemSage optimizer,[21] which is able to process density data directly (i.e., without prior conversion to apparent molar volumes). For this temperature range, the volumetric

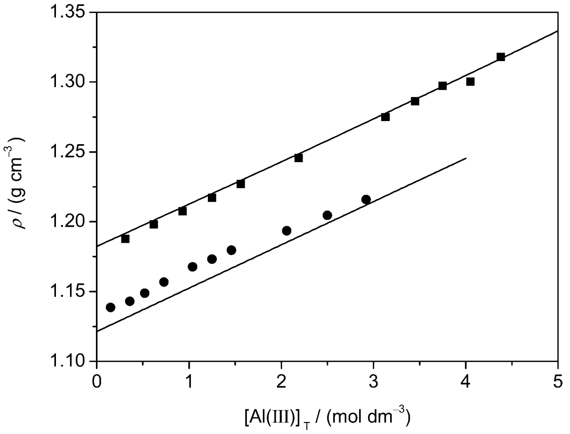

Figure 9. Densities of isomolar series of NaOH/NaAl(OH)$_4$ mixtures at constant ionic strengths (i.e., total NaOH concentrations) at 75 °C. Experimental data were taken from Li et al.[7] Squares, $I = 6$ mol dm^{-3}; dots, $I = 4$ mol dm^{-3}. Solid lines, present Pitzer model.

Pitzer parameters of hypothetical pure NaAl(OH)$_4$ could be represented by

$$\beta^{(0)V}/\text{kg mol}^{-1}\text{ bar}^{-1} = \frac{0.585540}{T/\text{K}} - 3.64456 \times 10^{-3} + 5.74765 \times 10^{-6}(T/\text{K}) \quad (5)$$

$$\beta^{(1)V}/\text{kg mol}^{-1}\text{ bar}^{-1} = \frac{-2.31281}{T/\text{K}} + 1.51194 \times 10^{-2} - 2.52255 \times 10^{-5}(T/\text{K}) \quad (6)$$

$$2C^{V}/\text{kg}^2\text{ mol}^{-2}\text{ bar}^{-1} = \frac{-8.19062 \times 10^{-2}}{T/\text{K}} + 5.12032 \times 10^{-4} - 8.07558 \times 10^{-7}(T/\text{K}) \quad (7)$$

As can be seen from Figures 4, 5, and 7, the volumetric Pitzer model for NaOH(aq)[19,20] predicts slightly lower densities when compared to the present experimental values, particularly at higher ionic strengths and temperatures (0.37% at $I = 6$ mol dm^{-3} and $t = 90$ °C). As already noted in the discussion of Figures 2 to 4, Figures 6 and 8 show a slight discrepancy between hypothetical NaAl(OH)$_4$ densities obtained by linear extrapolation and values resulting from the present Pitzer model. Nevertheless, Young's rule and the Pitzer model are essentially equivalent for the NaOH + NaAl(OH)$_4$ + H$_2$O system, although the latter may give better results at 90 °C.

The volumetric Pitzer model derived in this work reproduces the present experimental density data very well, including the slight curvature observed for mixtures represented on the molality scale (Figures 2 to 4, solid lines). However, it should be noted that extrapolations outside the temperature range of parametrization might not be well represented by the power series functions employed here.

Model Validation and Conclusions

The current volumetric Pitzer model was tested by comparison with experimental density data taken from the literature.[3,6,7] Lundquist's results[6] ($I < 4$ mol kg^{-1} and A/C < 0.6, method not reported) appear to be systematically higher than the calculated values by about 0.5%. Agreement of the data by Li et al.[7] ($I < 8$ mol kg^{-1} and A/C < 0.7, pycnometry) with the model is significantly better at $I = 6$ mol dm^{-3}, whereas their data at $I = 4$ mol dm^{-3} do not extrapolate to the correct NaOH(aq) density (Figure 9). It should be noted that the sodium hydroxide samples used in these two studies[6,7] have been reported to contain 0.5% and 1% Na$_2$CO$_3$, respectively. The earlier data of Ikkatai and Okada[3] ($I < 8$ mol kg^{-1} and A/C < 0.65, pycnometry) generally agree well (to better than 0.5%) with the model calculations, except for the highest concentrations studied. Because the concentrations reported in these studies have been given in various volumetric units, the modeling software described in part 1 of this series[2] that performs all unit conversions internally has been used.

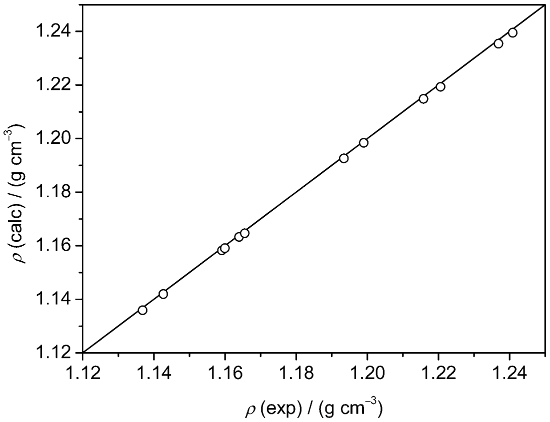

Figure 10. Predicted vs experimental densities of twelve 7-component synthetic Bayer liquors at 25 °C. (See the text.) Perfect agreement is indicated by the straight line.

The present volumetric Pitzer model has been further validated by predicting the densities of 12 carefully prepared and characterized 7-component synthetic Bayer liquors. The deviations between predicted and measured densities were (−0.08 ± 0.02)%, indicating the good performance of the current model for these multicomponent electrolyte mixtures (Figure 10).

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