Densities of Concentrated Alkaline Aluminate Solutions at Temperatures from (323 to 573) K and 10 MPa Pressure

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Densities of highly alkaline sodium aluminate solutions have been measured by vibrating-tube densimetry over the temperature range $323 \leq T/K \leq 573$ at a pressure of 10 MPa. Ionic strengths, I, of these mixed solutions were $1 \leq I/\text{mol} \cdot \text{kg}^{-1} \leq 6$, and the degree of substitution of hydroxide by aluminate, α, ranged from $0.1 \leq \alpha \leq 0.4$, where $\alpha = m_A/m$ and m_A and $m (= I)$ are the aluminate and total molalities, respectively. Apparent molar volumes, V_ϕ, derived from the density data for the $(\text{NaOH} + \text{NaAl(OH)}_4)(\text{aq})$ solutions, were found to follow Young's rule; that is, they depended linearly on the level of substitution of aluminate for hydroxide at all temperatures. The slopes of the Young's rule plots were independent of ionic strength at a given temperature but depended linearly on temperature. It is therefore possible to model V_ϕ (and hence the densities) of ternary $(\text{NaOH} + \text{NaAl(OH)}_4)(\text{aq})$ mixtures using only two parameters in addition to those needed for the correlation of the binary NaOH(aq) solutions. This also means that the standard state (infinite dilution) partial molar volumes, $V_2°$, of pure, hypothetical NaAl(OH)$_4$(aq) can readily be obtained from $V_2°$ for NaOH(aq) by linear extrapolation using the two Young's rule parameters.

1. Introduction

In alumina refineries using the Bayer process, concentrated highly alkaline sodium aluminate solutions are continuously recycled to dissolve the aluminum-containing minerals in the bauxite ore upon heating and then to precipitate purified aluminum hydroxide (gibbsite) on cooling. The digestion stage of modern Bayer plants is being carried out at increasingly high temperatures (up to about 560 K) so as to better utilize ores containing boehmite and diaspore, whose solubilities and rates of dissolution are uneconomically low in the more common low-temperature plants (which typically operate at about 410 K). Precise knowledge of Bayer process solution densities over the entire industrial range of concentrations and temperatures is important for both process control and engineering design purposes (e.g., for sizing and for mass and energy transfer calculations). As a result of their compositional variability, it is not possible to characterize plant liquors experimentally under all conditions, and so such properties are commonly calculated using empirical models. The limitations of such models are well-known. As discussed elsewhere,[1] a better approach is to develop a thermodynamically consistent model of the major components in Bayer liquors, which can then be used for the reliable and robust prediction of process solution properties over wide ranges of conditions.

Similar model predictions are also required for certain nuclear waste treatment plants and storage facilities and in many geochemical situations where aluminum-containing minerals come into contact with highly alkaline aqueous solutions. Solution densities are also required to calculate the pressure dependence of thermodynamic quantities,[1] which can become significant at the elevated temperatures found in many chemical, hydrometallurgical, and geological processes.

In a previous paper,[2] we determined the densities of NaOH(aq) at ionic strengths up to about 8 mol·kg^{-1} and temperatures up to 573 K at a pressure of 10 MPa, using a purpose-built vibrating-tube densimeter. The present work extends these measurements to ternary (NaOH + NaAl(OH)$_4$)(aq) mixtures. It is noteworthy that binary sodium aluminate solutions, NaAl(OH)$_4$(aq), are unstable with respect to the precipitation of aluminum oxo/hydroxide solids, so that sodium aluminate only exists in solutions containing significant concentrations of NaOH(aq).

Despite the industrial, environmental, and geochemical importance of concentrated alkaline sodium aluminate solutions, quantitative information on their densities is limited.[3−11] Even for the temperature range $298.15 < T/K \leq 373.15$, there are relatively few papers in the open literature that report experimental density data for (NaOH + NaAl(OH)$_4$)(aq).[4,6,8−11] At higher temperatures (up to 623 K), only the low-precision data of Dibrov et al.,[7] at approximately saturation pressure, are available.

Accordingly, the present paper reports measurements of the densities of (NaOH + NaAl(OH)$_4$)(aq) over the temperature range $323.15 \leq T/K \leq 573.15$ at a pressure of (mostly) 10 MPa, and at ionic strengths $1 \lesssim m/\text{mol} \cdot \text{kg}^{-1} \lesssim 6$ with degrees of substitution of hydroxide by aluminate, α, of up to 0.4, where $\alpha = m_A/m$ and m_A is the aluminate molality. These limits, together with robust extrapolations of the data to higher (supersaturated) aluminate contents, cover most of the range of conditions of industrial interest in both low- and high-temperature Bayer plants.

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2. Experimental Section

2.1. Densimeter. The construction and operation of the vibrating-tube densimeter, which is capable of measurements up to 573 K at pressures up to 30 MPa, have been presented in detail previously,[2] so only a brief description is given here. The most important features of the densimeter are: (i) a Pt-10 % Rh vibrating tube, to cope with the corrosive nature of the present solutions; (ii) an optical vibration-detection system with light from a photodiode passing through quartz optical leads to a photodetector; (iii) one passive and four independent active heating units that provide a temperature stability of $\pm$ 2 mK during individual experiments and $\pm$ 10 mK over long periods (about 12 h); (iv) a high pressure fluid delivery system comprising a high-performance liquid chromatography (HPLC) pump and two sample loops that can be used singly or in series; use of two sample loops allows sodium aluminate samples to be preceded by and flushed out with NaOH solution to prevent precipitation of $Al(OH)_3(s)$; and (v) a backpressure regulator and two nitrogen-filled 500 mL stainless steel cylinders at the target pressure, connected in series, which act as passive pressure buffers. The densimeter works in a flow regime and measures density differences between an aqueous solution and water with a precision of better than $\pm$ 0.2 %, with a high throughput (about 30 min per sample), low sample consumption (about 20 mL per measurement), and short residence time (about 1 min) in the hot zone.[2]

As in our earlier study of NaOH(aq),[2] calibrations were carried out using water (with densities calculated from IAPWS-95)[12] and appropriate concentrated aqueous solutions of sodium chloride as the reference substances at $T \leq$ 523.15 K. The densities of the latter were calculated using the extended Pitzer formulation of Archer.[13] For reasons discussed previously,[2] nitrogen was used as the second reference substance[14] at 573.15 K. The calibration constant of the densimeter, determined with water and NaCl(aq) solutions, was found to be reproducible to $\pm$ 0.1 %.[2] As discussed in detail previously,[2] the overall accuracy of the reported densities at 573.15 K was estimated to be $\pm$ 0.1 % but is up to an order of magnitude better at lower concentrations (where the solution density approaches that of pure water) and lower temperatures (where the experimental and calibration uncertainties are lower).[2]

2.2. Solution Preparation. All solutions were prepared using degassed, CO_2-free high purity water (Millipore Milli-Q system, boiled and cooled under high purity nitrogen gas). Calibration solutions were prepared by weight, with buoyancy corrections, from analytical grade sodium chloride (Univar, assay $\geq$ 99.90 %, Ajax Finechem, Australia) and dried overnight under vacuum at 523 K.

Aqueous (NaOH + NaAl(OH)$_4$) solutions were prepared by weight from appropriate stock solutions, without buoyancy corrections, with a consequent accuracy of $\pm$ 0.1 %. Sodium hydroxide solutions, with carbonate impurities of < 0.1 % (by moles) of the total alkalinity, were prepared as described previously.[2] Sodium aluminate solutions were prepared by dissolving high-purity Al wire (BDH AnalaR, assay $\geq$ 99.9 %) in about 8 mol·kg^{-1} NaOH(aq). As the concentrations of these solutions are critical for high-precision density measurements, the method used previously[15] was modified to ensure an inert (N$_2$) atmosphere throughout, to shorten the dissolution time from 3 days to a few hours, and to have better control of the reaction rate.

Accordingly, aluminum wire was twisted into a "rope" about 20 cm long and 0.5 cm diameter, which was cut into about 1 cm lengths with stainless steel scissors. These Al chunks were washed with analytical reagent (AR) acetone and AR ethanol, dried overnight at 110 °C, and then stored in a desiccator. The reaction vessel was a 1 L screw-cap polypropylene bottle (Nalgene) with a threaded Teflon adapter joined to a 40 cm long vertically mounted condenser with a side arm near its top. Appropriate amounts of water and about 8 mol·kg^{-1} NaOH(aq) were weighed accurately into the preweighed bottle containing a magnetic stirrer bar and closed with its usual screw cap (a spacer separated the balance pan and bottle to minimize magnetic interference). The bottle was then placed in a water bath on a stirrer/hot plate, and the Teflon adapter and condenser were fitted. The condenser was flushed with humidified N$_2$, and the side arm was connected in series to a Dreschel bottle containing phenolphthalein solution and a soda-lime CO_2 trap.

The reaction vessel was heated to 70 °C with stirring, whereas the condenser was connected to a circulating thermostat set at 3 °C to minimize water loss during the reaction. An accurately known amount of Al was added, a few chunks at a time, through the condenser top, while maintaining a blanket of N$_2$. As the Al dissolution process is exothermic, the hot plate could be turned off once the reaction commenced. Ice cubes were added to the water bath if needed to moderate the reaction rate. After all of the Al had dissolved, the water bath was raised to 100 °C for 30 min to convert possible polymeric species to $Al(OH)_4^-$. The reaction vessel was then cooled to room temperature and weighed accurately. Finally, the alkaline sodium aluminate solution was filtered (0.45 μm membrane) under N$_2$. Water loss (as vapor) was typically < 0.5 % of the total mass of the solution and was taken into account in the calculations. The condenser and outlet tube were rinsed into the phenolphthalein solution and titrated with standard HCl. No significant loss (< 0.003 % by moles) of NaOH was detected. All solutions were stored under N$_2$ prior to the density measurements.

3. Results and Discussion

3.1. Densities of Alkaline Sodium Aluminate Solutions. The experimental densities of (NaOH + NaAl(OH)$_4$)(aq) solutions obtained in the present work at P = 10 MPa are collected in Table 1. Limited data were measured at T = 323.15 K and P = 2 MPa (Table 1). As discussed for NaOH(aq),[2] densities in Table 1 are reported at rounded conditions because the experimental temperatures and pressures were within $\pm$ 0.05 K and $\pm$ 0.05 MPa ($\pm$ 0.15 MPa at 323.15 K) respectively of the stated values. Multiple entries at constant concentration are repeat measurements (using the same calibration) of the same solution to establish measurement precision. The experimental density differences $\Delta\rho$ ($= \rho - \rho_w$) are essentially constant over these small temperature and pressure intervals. The reported densities, ρ, are based on the density of pure water, ρ_w, calculated from the IAPWS-IF97 "industrial formulation".[16,17] For convenience, these ρ_w values,[16] which agree with those calculated from IAPWS-95[12] within a few ppm over the entire temperature range of interest, are also given in Table 1. Values of the measured quantity, $\Delta\rho$, which is independent of the model selected for ρ_w, can be calculated readily by subtraction using the data in Table 1.

3.2. Apparent Molar Volumes of Alkaline Sodium Aluminate Solutions. Apparent molar volumes, V_ϕ, of (NaOH + NaAl(OH)$_4$)(aq) solutions were calculated from the experimental densities (Table 1) using the usual relationship and assuming SI units:

$$V_\phi = (M'/\rho) - (\rho - \rho_W)/(m\rho\rho_W) \qquad (1)$$

In eq 1, M' is the average molar mass of the solute given by:

Table 1. Total (NaOH + NaAl(OH)$_4$), m, and NaAl(OH)$_4$, m_A, Molalities, Experimental Densities, ρ, Apparent Molar Volumes, V_ϕ, and Differences in Apparent Molar Volumes, $\Delta V_\phi = V_\phi$(exptl) − V_ϕ(calcd, eqs 3 and 4), of Ternary (NaOH + NaAl(OH)$_4$)(aq) Mixtures

Table 1. Continued

m	m_A	ρ	V_ϕ	ΔV_ϕ
mol·kg^{-1}	mol·kg^{-1}	g·cm^{-3}	cm^3·mol^{-1}	cm^3·mol^{-1}
T = 323.15 K, P = 2 MPa, ρ_w = 0.988872 g·cm^{-3}				
1.0238	0.1020	1.033290	3.769	0.031
1.0238	0.1020	1.033298	3.762	0.024
1.0037	0.4006	1.041322	17.562	−0.066
1.0037	0.4006	1.041329	17.556	−0.073
5.9990	0.6021	1.207842	9.036	0.072
5.9990	0.6021	1.207860	9.034	0.070
5.9974	2.3985	1.241657	23.009	0.126
5.9974	2.3985	1.241732	22.997	0.114
T = 323.15 K, P = 10 MPa, ρ_w = 0.992309 g·cm^{-3}				
1.0081	0.1051	1.035990	4.308	−0.066
1.0136	0.2044	1.039124	8.835	−0.075
1.0060	0.3014	1.041651	13.386	−0.065
1.0060	0.3014	1.041699	13.340	−0.112
1.0000	0.3991	1.044309	17.930	−0.134
1.0000	0.3991	1.044296	17.943	−0.121
2.0064	0.2007	1.075687	5.506	−0.003
2.0064	0.2007	1.075663	5.517	0.008
2.0064	0.4030	1.081194	10.192	−0.001
2.0102	0.6001	1.086588	14.744	0.005
2.0144	0.7997	1.092051	19.291	−0.028
4.0076	0.4025	1.147686	7.634	0.033
4.0017	0.8038	1.156801	12.311	0.048
4.0077	1.2008	1.165837	16.927	0.070
4.0255	1.6172	1.175419	21.690	0.071
6.0022	0.6043	1.210326	9.292	0.011
5.9948	1.1997	1.221905	13.922	0.025
6.0015	1.7970	1.233389	18.544	0.028
6.0395	2.3688	1.244659	22.885	0.028
T = 373.15 K, P = 10 MPa, ρ_w = 0.962932 g·cm^{-3}				
1.0124	0.1016	1.006110	3.511	0.066
1.0163	0.2016	1.009150	8.168	0.021
1.0596	0.3246	1.014265	13.390	−0.003
1.0126	0.4021	1.014685	17.633	−0.023
2.0458	0.2051	1.046699	5.059	0.071
2.0146	0.4015	1.050862	9.723	0.032
2.0109	0.6076	1.056122	14.619	0.009
2.0256	0.8095	1.061797	19.292	−0.006
4.0007	0.4031	1.116182	7.235	0.036
4.0239	0.8054	1.125980	12.017	0.034
4.0692	1.2438	1.136882	17.105	0.026
4.0495	1.6200	1.144207	21.600	0.020
6.3006	0.5705	1.185462	8.757	0.010
6.3006	0.5705	1.185532	8.747	0.000
6.0159	1.2093	1.190302	13.801	−0.006
6.0121	1.8033	1.201132	18.523	−0.019
6.1792	2.5462	1.218242	23.994	−0.053
6.1792	2.5462	1.218272	23.990	−0.057
T = 423.15 K, P = 10 MPa, ρ_w = 0.922319 g·cm^{-3}				
1.0021	0.1017	0.966872	−0.302	0.032
1.0036	0.2019	0.969726	4.617	−0.005
1.0133	0.3015	0.972833	9.408	−0.021
1.0280	0.4067	0.976253	14.314	−0.025
2.0156	0.2040	1.007845	1.874	0.041
2.0047	0.4011	1.012462	6.765	0.045
2.0047	0.4011	1.012500	6.745	0.025
2.0149	0.6080	1.018039	11.814	0.027
2.0318	0.8223	1.023894	16.959	0.028
2.0318	0.8223	1.023872	16.971	0.040
4.0165	0.4087	1.080241	4.911	0.038
4.0165	0.4087	1.080241	4.911	0.038
4.0094	0.8047	1.088589	9.821	0.044
3.9993	1.2010	1.096619	14.745	0.036
4.0400	1.5929	1.105819	19.448	0.021
5.9938	0.5994	1.141989	7.060	0.000
5.9938	0.5994	1.142029	7.053	−0.007
6.0107	1.2061	1.154269	11.963	−0.111
6.0006	1.8010	1.164029	16.955	−0.049
6.0060	2.3994	1.174309	21.859	−0.083
T = 473.15 K, P = 10 MPa, ρ_w = 0.870946 g·cm^{-3}				
1.0052	0.1021	0.919222	−7.853	0.017
1.0052	0.1021	0.919184	−7.806	0.064
1.0052	0.1021	0.919238	−7.873	−0.002
1.0052	0.1021	0.919199	−7.825	0.046
1.0031	0.2008	0.921765	−2.775	0.032
1.0031	0.2008	0.921803	−2.822	−0.015
1.0031	0.2008	0.921841	−2.869	−0.062
1.0031	0.2008	0.921502	−2.449	0.358
1.0098	0.3023	0.924721	2.384	0.056
1.0098	0.3023	0.924819	2.264	−0.065
1.0098	0.3023	0.924815	2.269	−0.060
1.0098	0.3023	0.924774	2.319	−0.009
1.0055	0.4002	0.927174	7.376	−0.013
1.0055	0.4002	0.927219	7.320	−0.069
1.0055	0.4002	0.927209	7.332	−0.056
1.0055	0.4002	0.927170	7.381	−0.008
1.0055	0.4002	0.927183	7.365	−0.024
1.0055	0.4002	0.927183	7.365	−0.024
1.0055	0.4002	0.927183	7.365	−0.024
2.0037	0.2005	0.961726	−4.383	0.044
2.0037	0.2005	0.961694	−4.364	0.063
2.0037	0.2005	0.961713	−4.375	0.052
2.0037	0.2005	0.961713	−4.375	0.052
2.0095	0.4049	0.967009	0.857	0.046
2.0095	0.4049	0.967022	0.849	0.038
2.0758	0.5970	0.974097	5.517	0.087
2.0758	0.5970	0.974196	5.460	0.030
2.0758	0.5970	0.974174	5.473	0.042
2.0758	0.5970	0.974174	5.473	0.042
2.0007	0.7999	0.976181	11.055	0.063
4.0066	0.4031	1.036827	0.298	0.079
4.0104	0.8058	1.045497	5.448	0.060
4.0101	1.2077	1.053674	10.600	0.053
4.0101	1.2077	1.053640	10.610	0.063
4.3843	1.5325	1.071503	13.757	0.030
4.3843	1.5325	1.071503	13.757	0.030
4.3843	1.5325	1.071529	13.751	0.023
6.0064	0.6035	1.100773	3.544	0.037
6.0064	0.6035	1.101149	3.478	−0.029
6.0064	0.6035	1.101017	3.501	−0.006
6.0064	0.6035	1.101197	3.469	−0.038
6.0127	1.2138	1.112237	8.691	−0.043
6.0127	1.2138	1.112277	8.684	−0.050
6.0030	1.7966	1.122037	13.651	−0.084
6.0030	1.7966	1.122067	13.646	−0.089
6.0030	1.7966	1.121937	13.669	−0.065
6.0079	2.4012	1.132297	18.746	−0.163
T = 523.15 K, P = 10 MPa, ρ_w = 0.805701 g·cm^{-3}				
1.0075	0.1017	0.860561	−22.908	−0.005
1.0075	0.1017	0.860548	−22.890	0.013
1.0044	0.2041	0.863153	−17.549	−0.059
1.0044	0.2041	0.863126	−17.511	−0.021
1.0051	0.2930	0.865531	−12.880	−0.094
1.0051	0.2930	0.865531	−12.880	−0.094
1.0113	0.3965	0.868547	−7.544	−0.160
1.0113	0.3965	0.868514	−7.498	−0.114
1.9968	0.1969	0.906406	−16.446	0.073
1.9968	0.1969	0.906406	−16.446	0.073
2.0441	0.4039	0.913260	−10.839	0.170
2.0441	0.4039	0.913305	−10.869	0.140
2.0692	0.5956	0.918882	−5.921	0.159
2.0692	0.5956	0.918857	−5.905	0.175
2.0138	0.7970	0.921247	−0.375	0.247
2.0138	0.7970	0.921296	−0.408	0.214
4.0111	0.4084	0.986964	−8.257	0.138
4.0111	0.4084	0.987004	−8.269	0.126
4.0214	0.8163	0.995734	−2.832	0.149
4.0214	0.8163	0.995696	−2.820	0.160
4.0118	1.1997	1.003043	2.265	0.165
4.0118	1.1997	1.003005	2.277	0.176
3.9991	1.5901	1.010146	7.485	0.181
3.9991	1.5901	1.010104	7.498	0.194
6.0050	0.5975	1.053773	−3.335	−0.037

Table 1. Continued

m	m_A	ρ	V_ϕ	ΔV_ϕ
mol·kg^{-1}	mol·kg^{-1}	g·cm^{-3}	cm^3·mol^{-1}	cm^3·mol^{-1}
6.0050	0.5975	1.053707	−3.322	−0.025
5.9999	1.1950	1.064214	1.933	−0.061
5.9999	1.1950	1.064284	1.919	−0.075
6.0109	1.8035	1.074839	7.283	−0.101
6.0109	1.8035	1.074814	7.288	−0.096
5.9979	2.4020	1.084907	12.405	−0.293
5.9979	2.4020	1.084993	12.388	−0.310
$T = 573.15$ K, $P = 10$ MPa, $\rho_w = 0.715290$ g·cm^{-3}				
1.0162	0.1031	0.784990	−61.125	−0.248
1.0162	0.1031	0.784982	−61.112	−0.234
1.0132	0.2049	0.787529	−55.757	−0.324
1.0132	0.2049	0.787552	−55.795	−0.363
1.0029	0.2953	0.789316	−50.969	−0.353
1.0029	0.2953	0.789295	−50.934	−0.318
0.9990	0.3923	0.791621	−45.721	−0.393
0.9990	0.3923	0.791621	−45.721	−0.393
2.0020	0.1952	0.838149	−45.565	0.000
2.0020	0.1952	0.838190	−45.597	−0.032
2.0033	0.3961	0.843132	−40.084	−0.013
2.0033	0.3961	0.843148	−40.096	−0.025
2.0355	0.6249	0.849990	−33.614	0.104
2.0355	0.6249	0.849990	−33.614	0.104
2.0042	0.8003	0.852611	−28.904	0.133
2.0042	0.8003	0.852634	−28.922	0.114
4.0048	0.3975	0.927581	−28.426	0.199
4.0048	0.3975	0.927628	−28.443	0.182
4.0048	0.3975	0.927594	−28.431	0.194
4.0048	0.3975	0.927640	−28.447	0.178
4.0217	0.8103	0.936635	−22.667	0.263
4.0217	0.8103	0.936658	−22.675	0.255
4.0545	1.2444	0.946433	−16.655	0.308
4.0545	1.2444	0.946408	−16.647	0.317
4.0019	1.6020	0.951327	−11.809	0.373
4.0019	1.6020	0.951305	−11.801	0.380
5.9970	0.5965	1.000034	−18.624	−0.079
5.9970	0.5965	1.000211	−18.662	−0.117
6.0111	1.2006	1.011323	−13.124	−0.120
6.0111	1.2006	1.011323	−13.124	−0.120
6.0015	1.7966	1.021069	−7.720	−0.124
6.0015	1.7966	1.021082	−7.723	−0.127
6.0174	2.4051	1.031254	−2.166	−0.121
6.0174	2.4051	1.031254	−2.166	−0.121

$$M' = (1 - \alpha)M_{NaOH} + \alpha M_{NaAl(OH)_4} \qquad (2)$$

where M_i is the molar mass of solute i, $\alpha = m_A/m$ is a convenient measure of the degree of substitution of hydroxide by aluminate, and m_A and m are the stoichiometric aluminate and total molalities, respectively. Apparent molar volumes so obtained are listed in Table 1.

As shown in Figure 1, the apparent molar volumes of (NaOH + NaAl(OH)$_4$)(aq) vary linearly upon substitution of hydroxide by aluminate, in accordance with Young's rule.[18] The slopes of these straight lines are essentially independent of ionic strength at a given temperature, while their intercepts correspond to the V_ϕ(NaOH, T) values reported previously,[2] which were measured at the same time. Because of this linear behavior, the apparent molar volumes of the ternary solutions, V_ϕ(NaOH + NaAl(OH)$_4$, T), can be described by eq 3:

$$V_\phi(NaOH + NaAl(OH)_4, T) = V_\phi(NaOH, T) + \alpha s(T) \qquad (3)$$

where V_ϕ(NaOH, T) is the apparent molar volume of NaOH(aq) at 10 MPa (or 2 MPa for the limited data measured at that pressure), given by eqs 4 to 8 of Hnědkovský et al.,[2] and $s(T)$ is the average slope of the Young's rule plots at temperature T. These slopes were correlated as a linear function of temperature,

Table 2. Apparent Molar Volumes of Pure, Hypothetical NaAl(OH)$_4$(aq) at Rounded Concentrations and Temperatures at 10 MPa Pressure, Calculated from Equations 3 and 4

T/K	323.15	373.15	423.15	473.15	523.15	573.15
m/mol·kg^{-1}	V_ϕ(NaAl(OH)$_4$, T)/cm^3·mol^{-1}					
0^a	43.32	42.86	38.31	27.39	1.61	−80.35
1	45.99	46.51	44.27	38.35	24.86	−12.10
2	47.32	48.02	46.43	41.88	31.45	3.76
4	49.40	50.26	49.45	46.50	39.35	20.60
6	51.07	52.06	51.75	49.80	44.50	30.71

^{a} Partial molar volumes at infinite dilution ($V_\phi(I = 0) \equiv V_2^\circ$).

$$s(T) = a + bT \qquad (4)$$

where a and b are temperature-independent parameters, with values: $a = (35.438 \pm 0.805)$ cm^3·mol^{-1} and $b = (0.03358 \pm 0.00201)$ cm^3·K^{-1}·mol^{-1} (Figure 2).

Equations 3 and 4 describe the apparent molar volumes of the ternary mixtures (Figure 3) to within $\pm$ 0.1 cm^3·mol^{-1} at temperatures up to 473 K, increasing to $\pm$ 0.3 cm^3·mol^{-1} at T = 523 K and to $\pm$ 0.4 cm^3·mol^{-1} at T = 573 K (these differences are also listed in Table 1). The corresponding experimental density differences $\Delta \rho$ agree with the model to within $\pm$ 0.3 % at $T \leq$ 523 K, becoming slightly worse at T = 573 K (Figure 4). This level of agreement is somewhat poorer than that obtained for NaOH(aq),[2] which can in part be explained by the additional compositional degree of freedom. In addition, small but systematic trends in the deviations can be observed in Figures 3 and 4 at the two highest temperatures. This means that the slopes in Figure 1, parts c and d, depend slightly (but irregularly) on the ionic strength. This effect is also indicated by the larger error bars for these temperatures shown in Figure 2. This behavior cannot be reproduced precisely by the present simple two-parameter model. For example, a purely empirical seven-parameter interpolation formula, which reproduces $\Delta \rho$ values to better than $\pm$ 0.3 % at all temperatures, has been used to calculate density differences between ternary alkaline sodium aluminate and binary sodium hydroxide solutions.[19] On the other hand, the present model, although slightly less precise, is more fundamental since it is based on Young's rule. It is also more robust because it is independent of ionic strength and depends only linearly on temperature. As such it provides a useful means of predicting densities of concentrated alkaline aluminate solutions even outside of the present experimental ranges. This is important for the Bayer process industry where highly supersaturated solutions, with up to about 75 % (by moles) substitution of hydroxide by aluminate, are common in high-temperature digestion plants.

Figure 5 shows that the present results at 10 MPa align smoothly with our earlier investigations of alkaline sodium aluminate solutions over the same compositional range at 298.15 $\leq T$/K $\leq$ 363.15 and P = 0.1 MPa.[3,4] This is expected since the compressibility of electrolyte solutions at low temperatures is generally rather small. Comparison of the present results with literature data at higher temperatures is problematic given that the only published study[7] is of relatively low precision (with a stated uncertainty in ρ of $\pm$ 0.5 %) and was performed at variable but unspecified ("somewhat higher" than saturation) pressure. Nevertheless, assuming that the densities reported by Dibrov et al.[7] correspond approximately to the saturation pressure of pure water, the present model agrees (for $m \leq$ 7.4 mol·kg^{-1}) with their values to $\leq$ 0.5 % at 323 K, rising to about 1 % at 573 K. Given the likely overall uncertainties in both data sets, this level of agreement is reasonable.

The simple linear (Young's rule) behavior shown by aqueous mixtures of (NaOH + NaAl(OH)$_4$) with respect to apparent
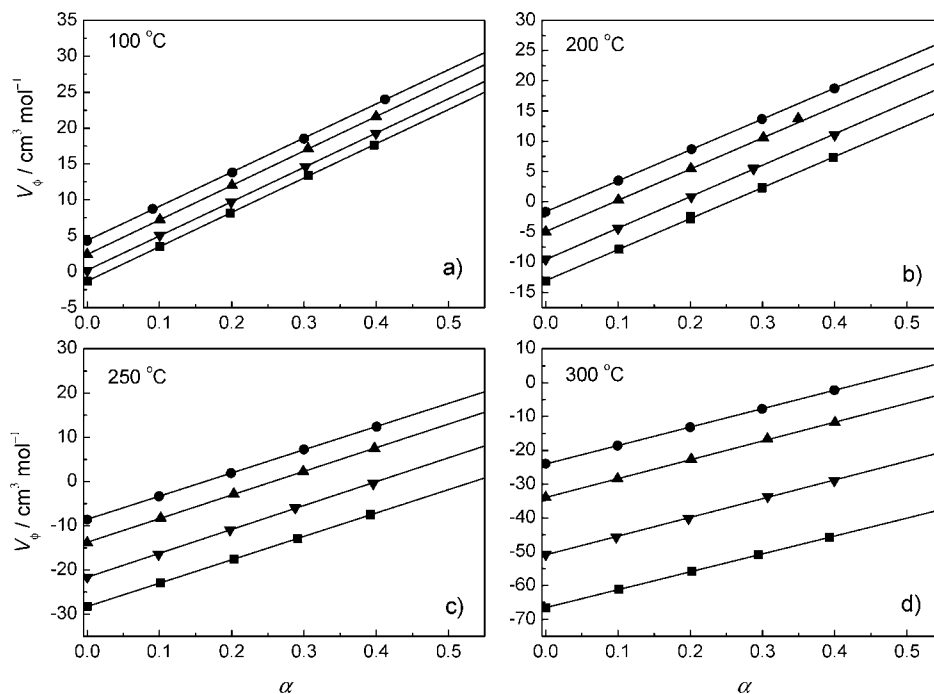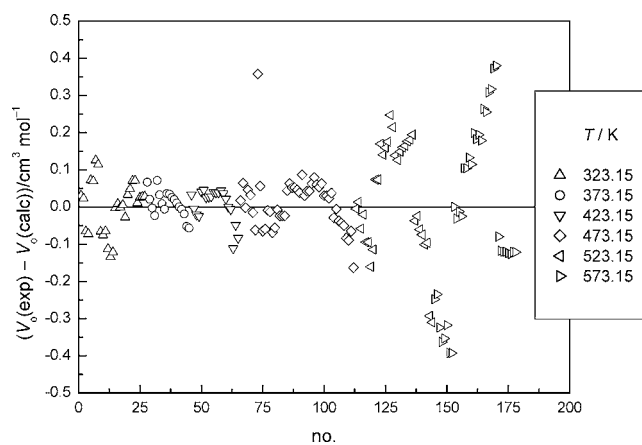
Figure 1. Linear dependence (Young's rule behavior) of apparent molar volumes of ternary alkaline sodium aluminate solutions, V_ϕ(NaOH + NaAl(OH)$_4$, T), with respect to the substitution of hydroxide by aluminate (α) at selected temperatures at $P = 10$ MPa and constant ionic strengths I/mol·kg^{-1} of: ■, 1; ▼, 2; ▲, 4; and ●, 6.
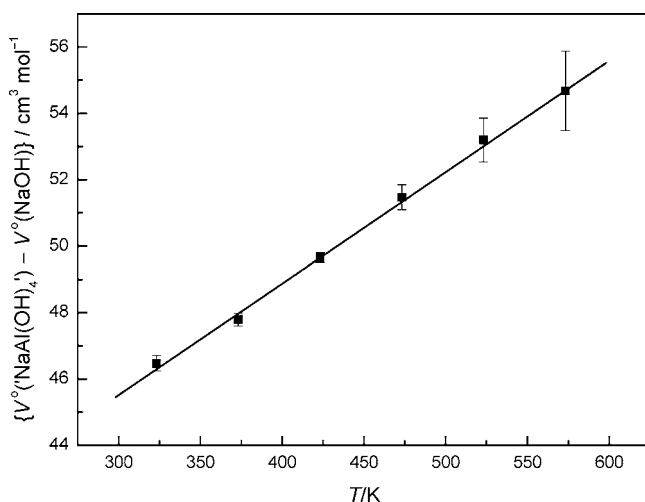
**Figure 2.** Temperature dependence of the average slopes, $s(T) = V°$(NaAl(OH)$_4$, T) $- V°$(NaOH, T), of the lines shown in Figure 1 (with standard deviations indicated by error bars).

Figure 3. Experimental apparent molar volumes of ternary alkaline sodium aluminate solutions, V_ϕ(NaOH + NaAl(OH)$_4$, T), at $P = (2$ and $10)$ MPa (points) compared with the values calculated from the present model (eqs 3 and 4, line). The data points are presented in the same order as in Table 1.
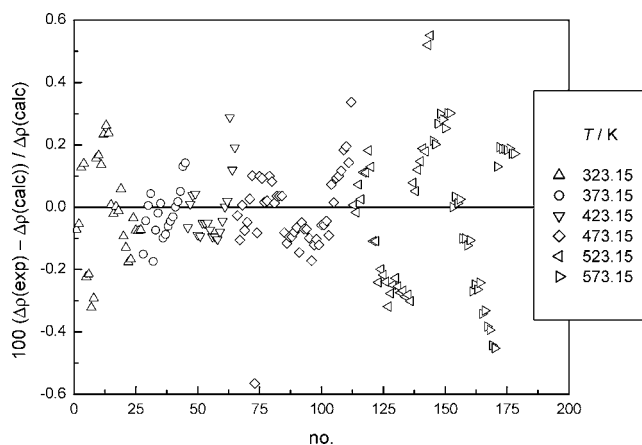
Figure 4. Relative density differences of (NaOH + NaAl(OH)$_4$)(aq) solutions measured in this work at $P = (2$ and $10)$ MPa (points) compared with the values calculated from the present model (eqs 3 and 4, line). The data points are shown in the same order as in Table 1.

molar volumes (Figure 1, eq 3) enables reliable estimates to be made for the V_ϕ values of pure, hypothetical NaAl(OH)$_4$(aq) solutions (for which $\alpha = 1$). Since the slopes $s(T)$ are independent of ionic strength, it is reasonable to assume that eq 3 is also applicable to partial molar volumes at infinite dilution. The $V_2°$ and V_ϕ values so obtained at rounded temperatures and ionic strengths are summarized in Table 2. Simple linear combination of these values with the corresponding values for NaOH(aq)[2] allows a reliable calculation of the densities of *any* mixture of (NaOH + NaAl(OH)$_4$)(aq) within the ionic strength/temperature matrix. As noted above, this includes supersaturated solutions, which are frequently encountered in the Bayer process but are difficult to characterize experimentally, especially by vibrating-tube densimetry (because of the possibility of tube blockage).
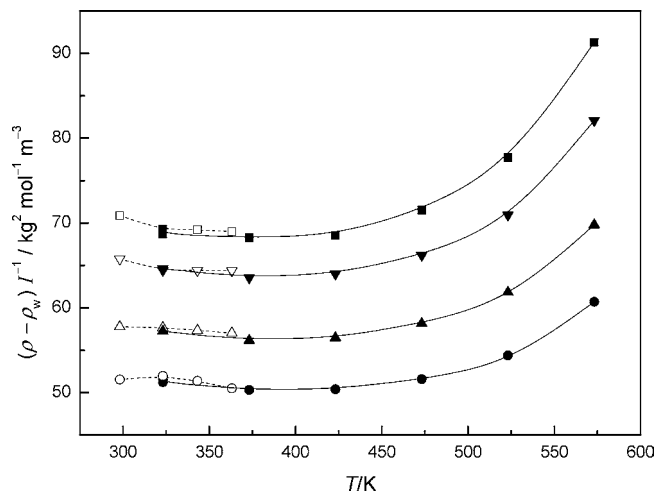
It should be noted that we have found analogous Young's rule behavior for the apparent molar heat capacities ($C_{p\phi}$) of

Figure 5. Density differences, $\Delta\rho$ ($= \rho - \rho_w$), weighted by ionic strength, of pure, hypothetical NaAl(OH)$_4$(aq) at $P = 10$ MPa, determined by extrapolation in this work (solid symbols) and literature values[3,4] at $P = 0.1$ MPa (open symbols). Data refer to constant ionic strengths, I/mol·kg^{-1}, of: ■, 1; ▼, 2; ▲, 4; and ●, 6. Lines were added as a visual aid.

(NaOH + NaAl(OH)$_4$)(aq) mixtures over the same conditions.[19] These and the present volumetric data have been incorporated into our 10 component synthetic Bayer liquor model,[4,17,20] which provides modeling capabilities for predicting the thermodynamic properties of Bayer process solutions employed in alumina production over wide ranges of temperature and concentration (pressure is not usually an industrially significant variable).

4. Conclusions

A purpose-built vibrating-tube densimeter has been used to measure densities of concentrated alkaline sodium aluminate solutions with an accuracy of $\lesssim 0.1$ % at temperatures up to 573 K and a pressure of 10 MPa. The apparent molar volumes calculated from these data showed simple linear mixing (Young's rule) behavior upon substitution of aluminate for hydroxide. These data enable the comprehensive thermodynamic modeling of the densities and related thermodynamic quantities for this geochemically and industrially important mixed electrolyte system to high concentrations, pressures, and temperatures.

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