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Viscosity, Density, and Refractive Index of Aqueous Sodium and Potassium Aluminate Solutions

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The viscosities, densities, and refractive indices of synthetic sodium and potassium aluminate solutions are reported as a function of aluminum and caustic concentration, total caustic to Al(III) molar ratio, and temperature. The influence of hydrogen isotope was also explored through complementary studies on deuterated solutions. A significant alkali metal ion effect on the viscosity and density is indicated, the influence of the other primary variables shown to range from strong to moderate. Under similar solution conditions, the sodium ions display stronger solute interactions and greater solution structure-making ability, reflected in higher solution viscosity (and enhanced density), than do potassium ions. The effect of Al(III) solute concentration, caustic to Al(III) ratio, ionic strength, and hydrogen isotope on the solution bulk properties is discussed and their relevance to speciation and the interactions of species in Bayer liquors is highlighted. Empirical models for viscosity and density are proposed.

Introduction

The physical properties of saturated and supersaturated caustic aluminate solutions (Bayer liquors), such as viscosity (η) and density (ρ), are largely determined by solution speciation and the interactions between solute species and solvent molecules, both of which are central to the precipitation of $Al(OH)_3$ from the liquors. Previously, the densities of fresh sodium aluminate liquors were employed to quantify solution structural changes (Zambo, 1986) and their viscosities used to reveal the mechanism of gibbsite nucleation (Buvari-Barcza et al., 1996). The use of solution viscosity data to facilitate the determination of the tetrahydroxo aluminate species (monomer, dimer, and hexamer) in concentrated sodium and potassium aluminate solution is exemplified by the speciation studies of Buvari-Barcza et al. (1996), Myund et al. (1995), and Eremin et al. (1974).

Despite their fundamental importance, published viscosity and density data of Bayer liquors are very limited. To date, the data reported by Ikkatai et al. (1963) for sodium aluminate solutions are the most useful information available. No property data (e.g. viscosity, density, and refractive index) for potassium aluminate solutions or deuterated solutions have been published. The property information on synthetic caustic aluminate solutions of industrial strength forms an important basis for benchmarking those of plant Bayer liquors that may contain various dissolved impurities.

In the present work we have measured the solution absolute viscosity, density, and refractive index as a function of Al(III) concentration, total caustic to Al(III) molar ratio, alkali metal ion type (Na^+ versus K^+), ionic strength of alkali ([NaOH] or [KOH]), and hydrogen isotope (H versus D) over the temperature range (22 to 75) °C. Empirical models describing the relationship between the viscosities or densities of the solutions and the primary variables were obtained.

Experimental Method

Fresh, pure, synthetic hydrogenated and deuterated sodium and potassium aluminate solutions were used in this study. They were prepared from aluminum metal (99.99% pure, 0.01% Si, Merck, Australia); sodium hydroxide (99.0% pure, 1.0% Na_2CO_3, Merck, Australia); sodium deuterioxide (40%, solution in D_2O, 99+ atom % D, Aldrich Chemicals, USA); potassium hydroxide (85.0% pure, 13.5% H_2O, 1.0% K_2CO_3, and 0.5% Na, Merck, Australia); potassium deuterioxide (40%, solution in D_2O, 98+ atom % D, Aldrich Chemicals, USA); Milli-Q water (specific conductivity $< 0.5\ \mu s\ cm^{-1}$, pH 5.6, and surface tension 72.8 mN m^{-1} at 20 °C), and deuterium oxide (99.9% D, Aldrich Chemicals, USA).

Stock solutions containing (4 or 6) M caustic (NaOH or KOH or NaOD or KOD) and (2.92 or 4.38) M Al(III) ([caustic]/[Al(III)] = 1.37) were first prepared as below and then diluted with Milli-Q water or D_2O or caustic solution to prepare the required solution. A known mass of NaOH or KOH or NaOD or KOD was dissolved in half of the required volume of Milli-Q or heavy water in a 1 dm^3, caustic-resistant polymethylpentane (PMP) vessel. This was followed by slow addition of a known mass of Al metal (previously washed with ethanol to remove any organic contamination). After complete dissolution, the solution was transferred to a volumetric flask and made up to the mark with Milli-Q water or D_2O, and the solution then was twice filtered through a caustic-resistant, 0.20 μm Teflon membrane. Prior to analysis, the solutions were stored in well-sealed PMP containers.

Dilution: optically clear caustic aluminate solutions containing Al(III) in the range (0−4.38) M, with a caustic to Al(III) molar ratio of 1.37, were prepared from the stock solution by dilution with Milli-Q water or D_2O, while the solutions containing Al(III) in the range (0−2.92 or 0−4.38) M, with a constant [caustic] = (4 or 6) M, were prepared from the stock solution by dilution with 4 M or 6 M caustic solution (NaOH, KOH, NaOD, or KOD). Al(III) and NaOH or KOH or NaOD or KOD concentrations were determined

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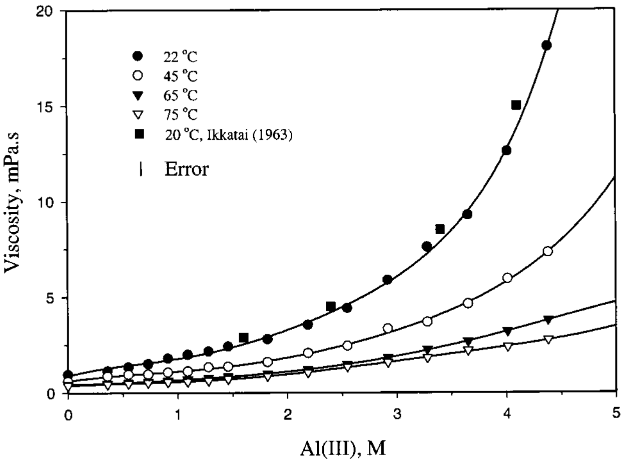

Figure 1. Absolute viscosity of sodium aluminate solutions as a function of Al(III) concentration at a constant [NaOH]/[Al(III)] = 1.37 and different temperatures. Model: eq 2.

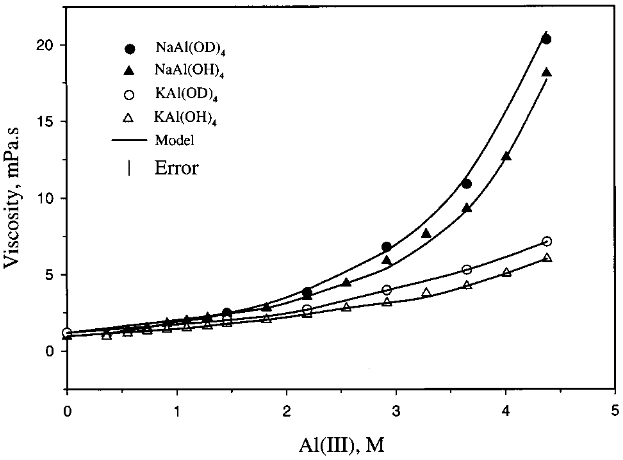

Figure 2. Absolute viscosity of caustic aluminate solutions as a function of Al(III) concentration at a constant [caustic]/[Al(III)] = 1.37 and 22 °C.

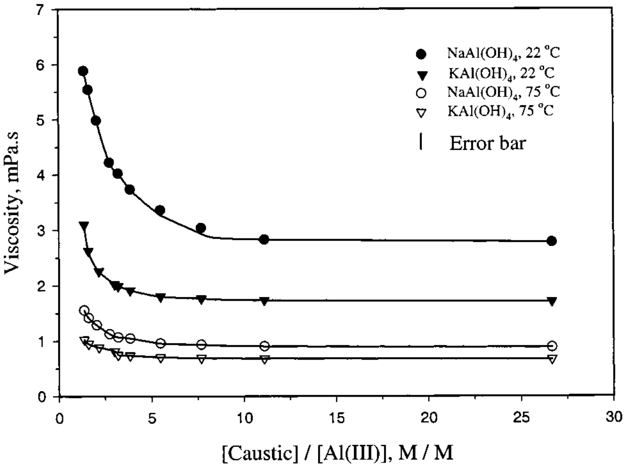

Figure 3. Absolute viscosity of caustic aluminate solutions as a function of [caustic]/[Al(III)] ratio at a constant [caustic] = 4 M and different temperatures. Model: eq 1.

by inductively coupled plasma atomic emission spectroscopy (ICP-AE, Spectro Analytical Instruments, SIM-SEQ).

A Haake CV20 concentric cylinder rheometer (Haake, Germany), fitted with a stainless steel Mooney-Ewart (45 mm diameter and gap) concentric cylinder sensor, was used to determine the shear stress versus the shear rate over the shear rate range (0−300) s^{-1} for concentrated solutions containing (0.40−4.38) M Al(III). A circulating oil bath was used to control the temperature within ±0.5 °C. The viscometer was calibrated using a standard instrument fluid (Brookfield Fluid 10). Shear stress versus shear rate curves for the solutions studied were effectively linear, and the flow behavior can be described as Newtonian with shear independent viscosities. The kinematic viscosities of the dilute solutions containing Al(III) < 0.4 M were measured using a precalibrated, Ostwald capillary viscometer (flow time of ≈20 min for Milli-Q water). Flow times were measured to within 0.01 s with a stopwatch. The viscometer was calibrated with Milli-Q water prior to every measurement. The reproducibility between replicate viscosities (3) was within ±2%.

Densities of the solutions were measured in triplicate with an accuracy of ±0.01% using a single-stem, graduated, precalibrated pycnometer of ~10 cm^3 volume provided with a well-fitted glass stopper to prevent evaporation. The pycnometer was calibrated with Milli-Q water prior to every measurement. A precision thermostat (accuracy ±0.05 °C) was used for temperature control during the measurements by the Ostwald capillary viscometer and pycnometer.

Refractive indices of the solutions were measured in triplicate using an Abbe High Accuracy 60/ED refractometer with temperature control to within ±0.1 °C. The precision of the refractive index determination was ±0.0001 refractive index unit.

Results and Discussion

Solution Viscosity. The typical absolute viscosity behavior of hydrogenated and deuterated caustic aluminate solutions at different temperatures is given in Figures 1−3 and Tables 1−9. The error bars shown in the figures indicate the estimated 95% confidence intervals on each experimental value. Increase of temperature or dilution with water leads to a significant reduction in the viscosity. The increase of viscosity with increasing Al(III) concentration is less pronounced at (75 and 65) °C than at 22 °C. This result implies that strong interactions between the solute species and solvent molecules (e.g. hydrogen bonding) exist in the solution and that this interaction weakens with increasing temperature. The viscosities are in good agreement with those reported for sodium aluminate solutions by Ikkatai et al. (1963) (Figure 1).

The effect of alkali metal ion and hydrogen isotope on the viscosity at (22 and 65) °C is clearly observed in Tables 1−5. The presence of Na$^+$ results in a significantly higher viscosity than does that of K$^+$, and D$^+$ instead of H$^+$ results in higher viscosity under similar solution conditions. The viscosity was found to be approximately 1.2 times higher for deuterated than hydrogenated liquors at similar concentrations at lower temperature (22 °C). However, no such difference in viscosity was observed for deuterated and hydrogenated aluminate solutions of K$^+$ at 65 °C or for the Na$^+$- and K$^+$-based aluminate solutions at 75 °C. These observations indicate that stronger Na$^+$ interactions with other solution species as compared with those of K$^+$ and a stronger deuterium effect in contrast to that of hydrogen prevail. Table 5 shows the linear increase of viscosity with increasing Al(III) concentration for dilute caustic aluminate solutions (Al(III) = 0−0.40 M) at (22 and 65) °C. The viscosities are higher for sodium than potassium aluminate solution at 22 °C but are similar for both alkali metal ion type solutions at 65 °C.

The viscosities of caustic-diluted aluminate solutions at different temperatures are shown in Figure 3 and Tables

Table 1. Absolute Viscosity of Sodium Aluminate Solutions As a Function of Al(III) Concentration at a Constant [NaOH]/[Al(III)] = 1.37 and Different Temperatures

	η/mPa·s			
Al(III)/M	22 °C	45 °C	65 °C	75 °C
4.38	18.080	7.307	3.798	2.763
4.01	12.610	5.949	3.211	2.397
3.65	9.273	4.636	2.688	2.205
3.28	7.611	3.683	2.263	1.828
2.92	5.877	3.340	1.829	1.578
2.55	4.416	2.442	1.480	1.358
2.19	3.546	2.071	1.216	1.058
1.82	2.801	1.604	1.010	0.877
1.46	2.422	1.363	0.855	0.722
1.28	2.167	1.338	0.778	0.638
1.09	1.998	1.130	0.706	0.593
0.91	1.798	1.065	0.648	0.567
0.73	1.525	0.976	0.582	0.533
0.55	1.345	0.959	0.540	0.495
0.36	1.149	0.869	0.495	0.452

Table 2. Absolute Viscosity of Potassium Aluminate Solutions As a Function of Al(III) Concentration at a Constant [KOH]/[Al(III)] = 1.37 and Different Temperatures

	η/mPa·s			
Al(III)/M	22 °C	45 °C	65 °C	75 °C
4.38	6.003	3.468	2.139	1.722
4.01	5.061	2.975	1.852	1.516
3.65	4.227	2.539	1.601	1.394
3.28	3.763	2.128	1.391	1.240
2.92	3.122	1.844	1.210	1.049
2.55	2.784	1.626	1.071	1.018
2.19	2.392	1.418	0.943	0.893
1.82	2.027	1.223	0.844	0.773
1.46	1.772	1.077	0.741	0.646
1.28	1.623	0.977	0.683	0.597
1.09	1.487	0.927	0.624	0.580
0.91	1.395	0.901	0.606	0.537
0.73	1.306	0.855	0.541	0.508
0.36	1.140	0.800	0.498	0.436

Table 3. Absolute Viscosity of Deuterated Sodium Aluminate Solutions As a Function of Al(III) Concentration at a Constant [NaOD]/[Al(III)] = 1.37 and Different Temperatures

[NaOD]/[Al(III)]/M/M		η/mPa·s			
	Al(III)/M	22 °C	45 °C	65 °C	75 °C
1.37	4.38	20.303	7.419	4.854	2.828
	3.65	10.877	4.736	3.218	2.013
	2.92	6.788	3.441	2.375	1.565
	2.19	3.818	2.031	1.698	1.174
	1.46	2.465	1.542	1.188	0.731
D_2O	0.00	1.186	0.709	0.507	0.442

Table 4. Absolute Viscosity of Deuterated Potassium Aluminate Solutions As a Function of Al(III) Concentration at a Constant [KOD]/[Al(III)] = 1.37 and Different Temperatures

[KOD]/[Al(III)]/M/M		η/mPa·s			
	Al(III)/M	22 °C	45 °C	65 °C	75 °C
1.37	4.38	7.110	3.406	2.093	1.756
	3.65	5.280	2.533	1.678	1.381
	2.92	3.952	2.060	1.242	1.026
	2.19	2.687	1.498	0.888	0.830
	1.46	2.001	1.111	0.722	0.687
D_2O	0.00	1.186	0.709	0.507	0.442

Table 5. Absolute Viscosity of Sodium and Potassium Aluminate Solutions As a Function of Al(III) Concentration (Lower Concentration) at a Constant [NaOH]/[Al(III)] or [KOH]/[Al(III)] = 1.37 and Different Temperatures

	η/mPa·s			
	$NaAl(OH)_4$		$KAl(OH)_4$	
Al(III)/M	22 °C	65 °C	22 °C	65 °C
0.365	1.1475	0.5048	1.0909	0.4950
0.292	1.1099	0.4907	1.0644	0.4826
0.219	1.0722	0.4773	1.0377	0.4709
0.146	1.0345	0.4632	1.0111	0.4590
0.109	1.0156	0.4564	0.9978	0.4532
0.073	0.9965	0.4494	0.9844	0.4471
0.035	0.9801	0.4469	0.9717	0.4434
0.029	0.9757	0.4449	0.9710	0.4417
0.023	0.9715	0.4429	0.9680	0.4400
0.018	0.9673	0.4409	0.9638	0.4384
0.012	0.9632	0.4389	0.9615	0.4368
0.006	0.9594	0.4370	0.9592	0.4355
0.000	0.9573	0.4353	0.9573	0.4353

Table 6. Absolute Viscosity of Sodium Aluminate Solutions As a Function of Al(III) Concentration at a Constant [NaOH] = 6 mol·dm^{-3} and Different Temperatures

[NaOH]/[Al(III)]/M/M		η/mPa·s			
	Al(III)/M	22 °C	45 °C	65 °C	75 °C
1.37	4.38	17.900	7.367	3.812	2.776
1.48	4.05	16.220	6.659	3.697	2.535
1.60	3.75	14.930	6.303	3.554	2.435
1.74	3.45	13.560	5.636	3.329	2.266
1.92	3.13	12.490	5.215	3.107	2.096
2.74	2.19	9.705	4.125	2.670	1.600
3.84	1.56	8.173	3.480	2.428	1.533
4.81	1.25	7.477	3.222	2.276	1.518
6.42	0.93	6.906	3.073	2.111	1.390
9.62	0.62	6.481	2.762	2.066	1.372
19.25	0.31	6.246	2.467	1.999	1.163

Table 7. Absolute Viscosity of Potassium Aluminate Solutions As a Function of Al(III) Concentration at a Constant [KOH] = 6 mol·dm^{-3} and Different Temperatures

[KOH]/[Al(III)]/M/M		η/mPa·s			
	Al(III)/M	22 °C	45 °C	65 °C	75 °C
1.37	4.38	6.074	3.493	2.101	1.725
1.48	4.05	5.470	3.243	1.946	1.563
1.60	3.75	4.981	3.078	1.850	1.482
1.74	3.45	4.580	2.854	1.803	1.408
1.92	3.13	4.258	2.830	1.748	1.335
2.74	2.19	3.364	2.246	1.474	1.202
3.84	1.56	2.985	2.160	1.333	1.112
4.81	1.25	2.680	2.075	1.264	1.076
6.42	0.93	2.522	1.944	1.218	1.040
9.62	0.62	2.395	1.814	1.174	0.951
19.25	0.31	2.176	1.535	1.148	0.863

6−9. The viscosities decrease dramatically upon increasing the [caustic]/[Al(III)] molar ratio from 1.37 to 5.0 over the temperature range (22−75) °C (Figure 3). Similar observations for sodium aluminate solutions were reported by Pearson (1955). Over the caustic dilution range studied, sodium aluminate solutions exhibit higher viscosities than potassium aluminate solutions, the difference in viscosities becoming smaller at higher temperature.

The influence of caustic concentration/ionic strength on viscosity is shown in Tables 6−9. The viscosities are higher for 6 M than for 4 M caustic aluminate solutions at 65 °C, and a similar trend has been observed at other temperatures. The difference between the viscosities at (4 and 6) M caustic concentrations is much larger for sodium than for potassium aluminate solution, indicating that alkali metal ion−aluminate/hydroxide ion specific interactions exist, the extent of which is both ionic strength and alkali metal ion dependent.

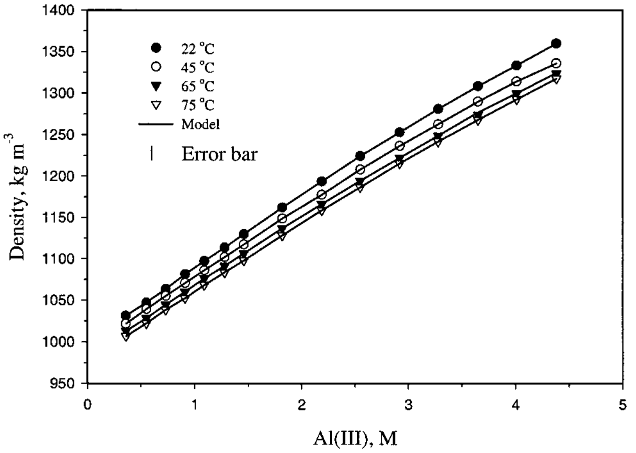

Figure 4. Density of sodium aluminate solutions as a function of Al(III) concentration at a constant [caustic]/[Al(III)] = 1.37 and different temperatures. Model: eq 4.

Table 8. Absolute Viscosity of Sodium Aluminate Solutions As a Function of Al(III) Concentration at a Constant [NaOH] = 4 mol·dm^{-3} and Different Temperatures

[NaOH]/ [Al(III)]/M/M	Al(III)/M	η/mPa·s			
		22 °C	45 °C	65 °C	75 °C
1.37	2.92	5.886	3.361	1.825	1.559
1.60	2.50	5.547	3.110	1.642	1.421
2.04	2.08	4.985	2.752	1.442	1.290
2.74	1.46	4.225	2.281	1.291	1.130
3.20	1.25	4.023	2.188	1.266	1.070
3.84	1.04	3.737	2.033	1.217	1.050
5.48	0.73	3.360	1.771	1.178	0.958
7.69	0.52	3.040	1.680	1.146	0.934
11.11	0.36	2.828	1.622	1.113	0.902
26.67	0.15	2.779	1.569	1.035	0.882

Table 9. Absolute Viscosity of Potassium Aluminate Solutions As a Function of Al(III) Concentration at a Constant [KOH] = 4 mol·dm^{-3} and Different Temperatures

[KOH]/ [Al(III)]/M/M	Al(III)/M	η/mPa·s			
		22 °C	45 °C	65 °C	75 °C
1.37	2.92	3.101	1.848	1.206	1.030
1.60	2.50	2.627	1.680	1.098	0.950
2.16	1.85	2.262	1.531	0.995	0.888
3.00	1.33	2.029	1.460	0.960	0.818
3.20	1.25	1.992	1.420	0.942	0.749
3.84	1.04	1.918	1.390	0.919	0.738
5.48	0.73	1.803	1.246	0.871	0.705
7.69	0.52	1.766	1.238	0.862	0.691
11.11	0.36	1.733	1.164	0.809	0.682
26.67	0.15	1.708	1.126	0.784	0.665

The observed behavior of the viscosity of both hydrogenated and deuterated caustic aluminate solutions is consistent with the fact that Na$^+$, in comparison with K$^+$, exhibits stronger ion-pairing ability (Moolenaar et al., 1970; Eremin et al., 1974; Sipos et al., 1997) and facilitates the formation of larger Al(III)-containing polymeric species (Myund et al., 1995) due to its higher charge density. The nature of the isotopic solvent also affects the solution viscosities. The isotope effect is consistent with the fact that D_2O has a higher viscosity than H_2O and a higher molar mass, moment of inertia, and intermolecular potential (Holtzer et al., 1969).

Solution Density. The typical behavior of the density of caustic aluminate solutions at different temperatures is shown in Figure 4 and Tables 10−18. Water dilution of concentrated caustic aluminate solutions leads to a greater reduction in density than increasing the temperature (Figure 4). The results agree well with the limited data reported for sodium aluminate solutions by Russell et al. (1955). For dilute solutions ([Al(III)] < 0.4 M), both temperature and water dilution have a profound effect on solution density while the effect of alkali metal ion is quite subtle (Table 14).

Table 10. Density of Sodium Aluminate Solutions As a Function of Al(III) Concentration at a Constant [NaOH]/[Al(III)] = 1.37 and Different Temperatures

Al(III)/M	ρ/kg·m^{-3}			
	22 °C	45 °C	65 °C	75 °C
4.38	1359.9	1336.1	1323.9	1317.8
4.01	1333.7	1314.6	1300.1	1293.0
3.65	1308.8	1290.1	1274.2	1268.1
3.28	1281.2	1263.0	1249.0	1242.0
2.92	1253.2	1236.6	1222.5	1215.7
2.55	1224.4	1208.0	1194.6	1186.8
2.19	1193.7	1177.8	1166.4	1158.7
1.82	1162.1	1148.7	1136.9	1128.3
1.46	1129.9	1117.3	1106.5	1098.0
1.28	1113.5	1102.1	1091.4	1083.5
1.09	1097.2	1086.2	1076.3	1068.4
0.91	1081.5	1070.7	1060.3	1052.6
0.73	1063.5	1055.1	1044.6	1038.5
0.55	1047.2	1039.4	1028.6	1022.2
0.36	1031.3	1021.8	1013.0	1006.8

Table 11. Density of Potassium Aluminate Solutions As a Function of Al(III) Concentration at a Constant [KOH]/[Al(III)] = 1.37 and Different Temperatures

Al(III)/M	ρ/kg·m^{-3}			
	22 °C	45 °C	65 °C	75 °C
4.38	1381.1	1367.2	1354.5	1347.0
4.01	1353.1	1339.8	1329.1	1320.0
3.65	1325.1	1312.3	1303.0	1293.4
3.28	1296.6	1286.0	1273.1	1264.2
2.92	1268.1	1256.1	1243.0	1234.5
2.55	1237.4	1224.9	1212.4	1204.2
2.19	1205.6	1194.0	1181.2	1174.1
1.82	1173.4	1161.1	1148.4	1141.9
1.46	1139.1	1128.3	1116.7	1109.7
1.28	1122.5	1111.8	1099.2	1093.6
1.09	1104.9	1094.7	1083.7	1076.9
0.91	1090.0	1079.6	1068.7	1062.5
0.73	1069.9	1060.5	1050.0	1043.6
0.36	1034.2	1025.6	1015.5	1009.4

Table 12. Density of Deuterated Sodium Aluminate Solutions As a Function of Al(III) Concentration at a Constant [NaOD]/[Al(III)] = 1.37 and Different Temperatures

[NaOD]/ [Al(III)]/M/M	Al(III)/M	ρ/kg·m^{-3}			
		22 °C	45 °C	65 °C	75 °C
1.37	4.38	1449.3	1432.9	1425.4	1419.2
	3.65	1400.6	1385.6	1376.6	1369.5
	2.92	1350.1	1338.1	1327.2	1320.1
	2.19	1293.4	1282.0	1270.1	1264.7
	1.46	1234.7	1222.9	1211.9	1205.0
D_2O	0.00	1104.8	1097.9	1087.5	1081.5

Table 13. Density of Deuterated Potassium Aluminate Solutions As a Function of Al(III) Concentration at a Constant [KOD]/[Al(III)] = 1.37 and Different Temperatures

[KOD]/ [Al(III)]/M/M	Al(III)/M	ρ/kg·m^{-3}			
		22 °C	45 °C	65 °C	75 °C
1.37	4.38	1482.0	1467.6	1456.8	1451.0
	3.65	1429.0	1416.5	1404.0	1499.0
	2.92	1370.1	1357.2	1346.0	1340.2
	2.19	1307.7	1296.5	1285.1	1279.1
	1.46	1242.0	1233.0	1221.4	1214.5
D_2O	0.00	1104.8	1097.9	1087.5	1081.5

Table 14. Density of Sodium and Potassium Aluminate Solutions As a Function of Al(III) Concentration (Lower Concentration) at a Constant [caustic]/[Al(III)] = 1.37 and Different Temperatures

	ρ/kg·m^{-3}			
	NaAl(OH)$_4$		KAl(OH)$_4$	
Al(III)/M	22 °C	65 °C	22 °C	65 °C
0.365	1031.6	1012.3	1033.6	1015.6
0.292	1024.9	1006.2	1026.7	1008.7
0.219	1018.2	1000.0	1019.6	1001.8
0.146	1011.5	993.7	1012.5	994.8
0.109	1008.1	990.5	1008.8	991.3
0.073	1004.7	987.2	1005.2	987.7
0.035	1001.3	984.0	1001.6	984.5
0.029	1000.7	983.4	1001.0	983.8
0.023	1000.1	982.9	1000.3	983.1
0.018	999.5	982.3	999.7	982.5
0.012	998.9	981.7	999.0	981.8
0.006	998.4	981.2	998.4	981.3
0.000	997.8	980.6	997.8	980.6

Table 15. Density of Sodium Aluminate Solutions As a Function of Al(III) Concentration at a Constant [NaOH] = 6 mol·dm^{-3} and Different Temperatures

[NaOH]/ [Al(III)]/M/M	Al(III)/M	ρ/kg·m^{-3}			
		22 °C	45 °C	65 °C	75 °C
1.37	4.38	1353.3	1336.2	1324.7	1318.0
1.48	4.05	1337.4	1324.1	1307.4	1300.3
1.60	3.75	1330.0	1318.6	1304.5	1297.3
1.74	3.45	1321.5	1308.9	1291.7	1286.2
1.92	3.13	1311.5	1300.0	1282.4	1275.0
2.74	2.19	1281.1	1269.9	1253.6	1245.5
3.84	1.56	1261.7	1249.0	1234.1	1227.0
4.81	1.25	1251.7	1237.2	1223.6	1217.2
6.42	0.93	1243.4	1227.1	1213.9	1207.4
9.62	0.62	1232.3	1218.3	1206.4	1198.2
19.25	0.31	1224.7	1209.0	1194.3	1187.7

Table 16. Density of Potassium Aluminate Solutions As a Function of Al(III) Concentration at a Constant [KOH] = 6 mol·dm^{-3} and Different Temperatures

[KOH]/ [Al(III)]/M/M	Al(III)/M	ρ/kg·m^{-3}			
		22 °C	45 °C	65 °C	75 °C
1.37	4.38	1381.1	1367.9	1354.5	1347.7
1.48	4.05	1370.4	1355.2	1344.7	1333.8
1.60	3.75	1359.2	1345.2	1338.2	1321.3
1.74	3.45	1353.6	1339.6	1326.7	1313.8
1.92	3.13	1344.1	1331.8	1313.2	1308.2
2.74	2.19	1316.0	1303.7	1292.5	1279.8
3.84	1.56	1296.3	1283.7	1272.0	1260.7
4.81	1.25	1286.5	1270.1	1258.8	1251.1
6.42	0.93	1277.8	1261.3	1249.0	1241.5
9.62	0.62	1268.6	1252.1	1238.7	1231.0
19.25	0.31	1258.9	1242.5	1225.9	1220.1

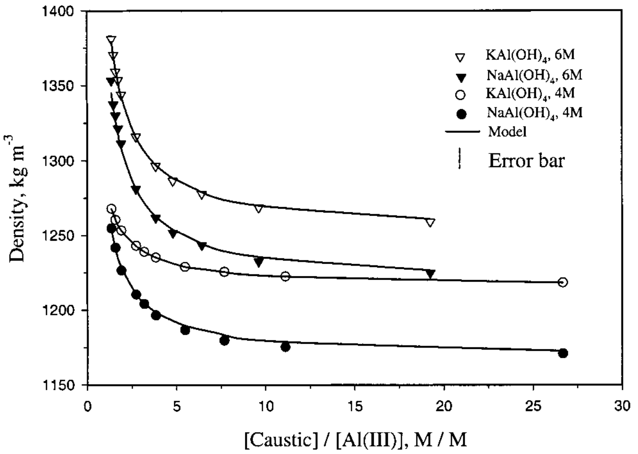

Figure 5. Density of caustic aluminate solutions as a function of [caustic]/[Al(III)] ratio at different ionic strengths and 65 °C. Model: eq 3.

Table 17. Density of Sodium Aluminate Solutions As a Function of Al(III) Concentration at a Constant [NaOH] = 4 mol·dm^{-3} and Different Temperatures

[NaOH]/ [Al(III)]/M/M	Al(III)/M	ρ/kg·m^{-3}			
		22 °C	45 °C	65 °C	75 °C
1.37	2.92	1253.7	1236.9	1223.4	1215.8
1.60	2.50	1241.7	1225.2	1213.7	1204.5
2.04	2.08	1226.4	1212.5	1202.5	1193.5
2.74	1.46	1210.3	1196.4	1186.5	1179.6
3.20	1.25	1204.0	1187.2	1182.3	1173.1
3.84	1.04	1196.4	1180.5	1175.0	1167.7
5.48	0.73	1186.6	1170.5	1163.1	1156.7
7.69	0.52	1179.6	1165.1	1155.2	1148.8
11.11	0.36	1175.4	1159.6	1149.4	1143.0
26.67	0.15	1170.8	1153.4	1140.9	1133.6

Table 18. Density of Potassium Aluminate Solutions As a Function of Al(III) Concentration at a Constant [KOH] = 4 mol·dm^{-3} and Different Temperatures

[KOH]/ [Al(III)]/M/M	Al(III)/M	ρ/kg·m^{-3}			
		22 °C	45 °C	65 °C	75 °C
1.37	2.92	1267.8	1256.0	1245.2	1234.9
1.60	2.50	1260.5	1247.7	1239.2	1229.4
2.16	1.85	1253.3	1241.1	1232.2	1220.4
3.00	1.33	1242.9	1229.9	1221.7	1211.5
3.20	1.25	1239.0	1226.8	1218.5	1209.5
3.84	1.04	1235.2	1223.2	1214.1	1207.5
5.48	0.73	1228.9	1216.6	1207.3	1201.5
7.69	0.52	1225.5	1213.4	1203.5	1198.5
11.11	0.36	1222.4	1210.9	1199.5	1194.5
26.67	0.15	1218.2	1205.3	1192.7	1187.6

At high ionic strength (>0.4 M), potassium-based deuterated and hydrogenated solutions have higher densities than sodium-based solutions with the difference becoming larger at higher Al(III) concentration. The average difference between the densities of potassium and sodium aluminate solutions of the same molarity is significantly less than the value one may predict on the basis of the atomic masses of potassium and sodium. This observation highlights the greater solution compaction ability of Na$^+$. The solution density decreases dramatically with increasing solution caustic to Al(III) molar ratios from 1.37 to 5.00 over the temperature range (22−75) °C. Furthermore, deuterated solutions exhibit higher density than hydrogenated liquors at similar concentrations, a finding which is consistent with the greater mass of the deuterium isotope.

Solution Refractive Index. The refractive indices of caustic aluminate solutions at different [caustic]/[Al(III)] ratios and water dilutions at 22 °C are shown in Figure 6 and Table 19, indicating a strong Al(III) concentration, [NaOH]/[Al(III)] ratio, and ionic strength dependency. An increase in the NaOH to Al(III) molar ratio leads to a significant increase in the solution refractive index. Alkali metal ion type did not have any noticeable effect on the solution refractive index, as shown by the limited data given in Figure 6. The results are in good agreement with the refractive indices reported by Counter (1996) for sodium aluminate solutions ([NaOH]/[Al(III)] = 1.37) at 25 °C.

Empirical Models for Viscosity and Density. To quantify the influence of each of the primary variables (Al(III) and caustic concentration, temperature, alkali metal ion, and hydrogen isotope) on the solution properties and provide convenient correlations for practical use, the viscosity and density data were fitted with empirical models (eqs 1−4). The model parameters were estimated by nonlinear regression analyses and are given in Table

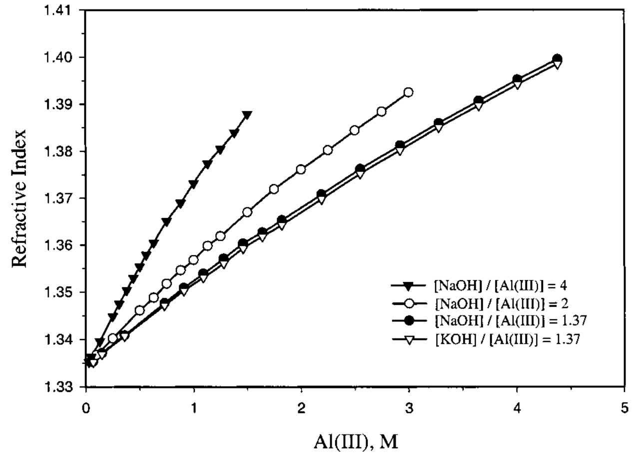

Figure 6. Refractive index of caustic aluminate solutions as a function of Al(III) concentration at a constant [caustic]/[Al(III)] = 1.37, 2, or 4 and 22 °C.

Table 19. Refractive Index of Sodium and Potassium Aluminate Solutions As a Function of Caustic or Al(III) Concentration at a Constant [caustic]/[Al(III)] Molar Ratio and 22 °C

	refractive index			
	$NaAl(OH)_4$		$KAl(OH)_4$	
[NaOH] or [KOH]/M	$x = 1.37$[a]	$x = 2$	$x = 4$	$x = 1.37$
6.00	1.3995	1.3925	1.3879	1.3985
5.50	1.3952	1.3884	1.3840	1.3942
5.00	1.3907	1.3844	1.3805	1.3897
4.50	1.3860	1.3802	1.3774	1.3851
4.00	1.3812	1.3761	1.3732	1.3802
3.50	1.3762	1.3719	1.3690	1.3752
3.00	1.3708	1.3670	1.3651	1.3698
2.50	1.3653	1.3619	1.3605	1.3643
2.25	1.3627	1.3598	1.3579	1.3618
2.00	1.3603	1.3566	1.3554	1.3593
1.75	1.3571	1.3546	1.3530	1.3561
1.50	1.3539	1.3516	1.3504	1.3531
1.25	1.3509	1.3484	1.3475	1.3503
1.00	1.3477	1.3461	1.3449	1.3472
0.50	1.3409	1.3402	1.3396	1.3407
0.20	1.3371	1.3367	1.3363	1.3369
0.10	1.3353	1.3353	1.3352	1.3352

[a] x = [NaOH]/[Al(III)] or [KOH]/[Al(III)] molar ratio.

20 for both caustic and water-diluted caustic aluminate solutions.

$$\eta_c = a_0 \exp\{(a_1[\mathrm{Al(III)}] + a_2[\mathrm{MOH}] + a_3M^{-1})(t + a_4)^{-1}\} \tag{1}$$

$$\eta_w = a_0 t^{-0.5} \exp\{a_1[\mathrm{Al(III)}] + a_2W^{0.5} + a_3M^{-1} + [\mathrm{Al(III)}](t + a_4)^{-1}\} \tag{2}$$

$$\rho_c = a_0 + a_1[\mathrm{Al(III)}] + a_2[\mathrm{MOH}] + a_3M + a_4t + [\mathrm{Al(III)}]^2t^{-1} \tag{3}$$

$$\rho_w = a_0 + a_1[\mathrm{Al(III)}] + a_2W + a_3M + a_4t + [\mathrm{Al(III)}]^2t^{-1} \tag{4}$$

where η_c = absolute viscosity of solution with caustic dilution, η_w = absolute viscosity of solution with water dilution (mPa·s), ρ_c = density of solution with caustic dilution (kg·m^{-3}), ρ_w = density of solution with water dilution (kg·m^{-3}), [Al(III)] = aluminum concentration (M), [MOH] = sodium or potassium hydroxide concentration (M), M = cation coefficient (Na^+ = 1 and K^+ = 2), W = hydrogen isotope type (H_2O = 1 and D_2O = 2), t = temperature (°C), and a_0–a_4 = parameters (Table 20). Appropriate units for the parameters may be derived such that each of the above model equations is dimensionally homogeneous.

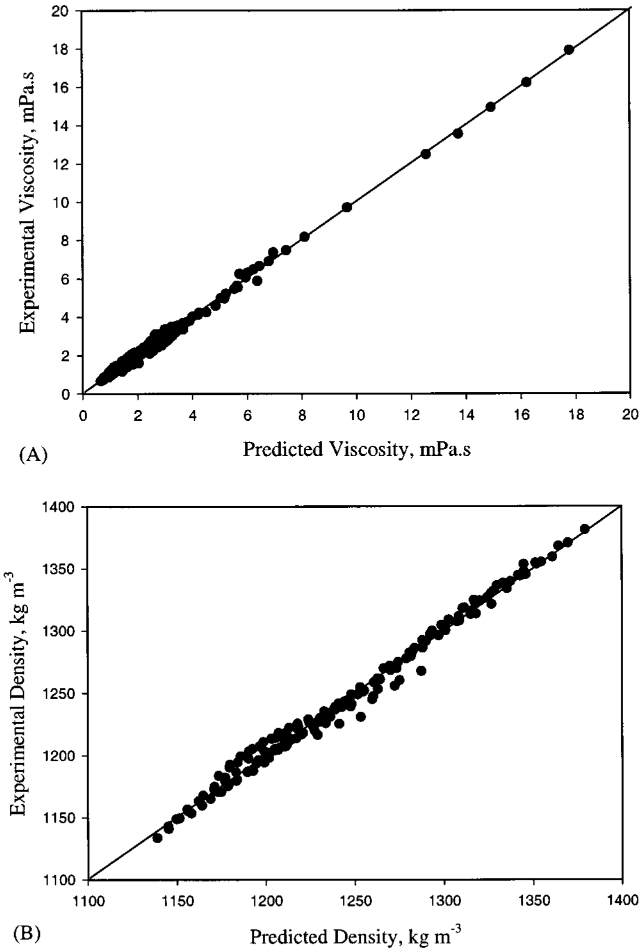

Figure 7. Comparison of the experimentally determined viscosity (A) and density (B) of the caustic aluminate solution upon caustic dilution with predicted values using eqs 1 and 3.

Table 20. Parameters Estimated for the Empirical Models for Viscosities and Densities of Caustic Aluminate Solutions (Eqs 1−4)

	equation			
parameter	1	2	3	4
a_0	0.130	0.110	1049.00	939.60
standard error	0.007	0.009	3.00	3.01
a_1	26.730	0.223	28.85	82.70
standard error	0.790	0.020	0.38	0.43
a_2	29.450	0.304	24.63	103.20
standard error	1.440	0.052	0.50	1.32
a_3	188.500	41.630	3.44	−25.77
standard error	6.500	0.929	0.92	2.34
a_4	76.280	1.382	−0.64	−0.57
standard error	2.410	0.086	0.02	0.03

Equations 1 and 2 show that the viscosity follows an exponential behavior with respect to the primary variables. The structure of the chosen models agrees with the empirical models reported previously for sodium aluminate solutions with NaOH dilution (Sato, 1954; Ikkatai et al., 1963).

The predictions of the models agree well, both qualitatively and quantitatively, with the experimental data

(Figures 1−5). Typical comparisons of the predicted and measured solution viscosities and densities are displayed in Figure 7, demonstrating the good agreement achieved and the adequacy of the models. It is pertinent to note that the models developed in the present work are found to be more comprehensive and simpler to use than those reported in the literature (Sato, 1954; Ikkatai et al., 1963).

Conclusions

The viscosities, densities, and refractive indices of pure synthetic sodium and potassium aluminate solutions have been measured and correlated as a function of aluminum and caustic concentration, alkali metal ion, caustic to aluminum molar ratio, hydrogen isotope, and temperature. A significant alkali metal ion effect on viscosity and density is shown, the influence of the other primary variables ranging from strong to moderate. Under similar solution conditions, sodium ions display stronger solute interactions and greater solution structure-making ability, reflected in higher solution viscosity (and enhanced density), than do potassium ions. The findings highlight the significant influence alkali metal ion, Al(III) solute concentration, ionic strength, and hydrogen isotope exert on solution species interactions and the bulk properties of dilute and concentrated Bayer liquors.

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