Heat Capacities of Concentrated Aqueous Alkaline Aluminate Solutions at 25 °C

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Heat capacities of aqueous $NaOH/NaAl(OH)_4$ solutions at total stoichiometric ionic strengths of up to 6 mol kg^{-1} and with up to 60 mol % substitution of OH^- by $Al(OH)_4{}^-$ have been measured at 25 °C using a Picker flow calorimeter. The mean apparent molar heat capacities ($C_{p\phi}$) of the $NaOH/NaAl(OH)_4$ mixtures were linear with respect to $Al(OH)_4{}^-$ substitution, consistent with Young's rule. This enabled $C_{p\phi}$ values to be derived for the hypothetical pure $NaAl(OH)_4(aq)$ solutions. The results so obtained are well described by a Pitzer model adapted from the literature, even up to high concentrations.

Introduction

The Bayer process, which is used for the extraction of gibbsite, $Al(OH)_3$, from bauxitic ores, may be summarized (simplistically) by the equilibrium

$$Al(OH)_3(s) + NaOH(aq) \Leftrightarrow NaAl(OH)_4(aq) \qquad (1)$$

Bauxitic ores typically contain a number of aluminum-bearing minerals and are digested with hot, concentrated sodium hydroxide solution.[1] After separation from undissolved solids, purified gibbsite is precipitated from the supersaturated alkaline aluminate solutions ("liquors") so produced by seeding and cooling. Because of the large temperature changes and the industrial magnitude of the Bayer process (many millions of tons per annum), reliable heat capacity data for concentrated $NaOH/NaAl(OH)_4$ solutions are required for a range of engineering purposes including heat exchanger designs, energy budgets, and so on.

The very few studies of the heat capacities of aqueous alkaline sodium aluminate solutions available in the open scientific literature are summarized in Table 1.[2−6] Perhaps uniquely among aqueous electrolyte solutions, there are more data available at higher temperatures than under ambient conditions. However, few of the published heat capacities can be considered to be of high quality. For near-ambient conditions, the most reliable data are undoubtedly those reported by Hepler and co-workers,[4] who used a Picker calorimeter to measure the heat capacities of $NaOH/NaAl(OH)_4$ solutions at temperatures from (10 to 55) °C. Unfortunately, their measurements were restricted to only two $[OH^-]/[Al(III)]$ ratios and the concentration ranges employed were generally below those of most interest industrially. For higher concentrations, only the approximate values of Mal'tsev and Mashovets,[2] obtained by static calorimetry, are available at temperatures close to 25 °C.

There is, therefore, a need for a detailed investigation of the heat capacities of aqueous alkaline sodium aluminate solutions at industrially relevant concentrations. The present study reports data at 25 °C, obtained using a Picker flow calorimeter and techniques described previously,[7] for $NaOH/NaAl(OH)_4$ mixtures at $1 \le I/\text{mol kg}^{-1} \le 6$ (where I is the total stoichiometric ionic strength, expressed in mol kg^{-1}) and at aluminate concentrations of up to $0.6I$.

Experimental Section

Solution Preparation. All solutions were prepared using high-purity water (Millipore MilliQ system) boiled and purged with nitrogen to remove traces of carbon dioxide; buoyancy corrections were applied throughout.

Concentrated stock solutions of sodium hydroxide (∼20 mol dm^{-3}) were prepared by dissolving solid sodium hydroxide (Univar, >97 mol % NaOH) in carbonate-free water. The resultant solution was allowed to stand for about one month in a tightly sealed Pyrex-glass container before being filtered (0.45 μm) to remove precipitated carbonate.[8] This solution was then analyzed (±0.2%) for hydroxide and carbonate by titration against hydrochloric acid (BDH, concentrated volumetric standard) using the Gran method.[9] The carbonate contamination was found to be less than 0.2% of the total alkalinity. The density of the concentrated NaOH solution at 25 °C was determined by vibrating tube densimetry (Anton Paar DMA 02D), and more dilute solutions were prepared by mass.

Concentrated stock solutions of alkaline sodium aluminate (∼5 mol dm^{-3} in aluminum and ∼8 mol dm^{-3} in NaOH) were prepared, as described in detail elsewhere,[10] by dissolving aluminum wire (99.9%, BDH, U.K.) in the appropriate mass of NaOH stock solution and water. After measurement of the densities of the two stock solutions, series of aqueous $NaOH/NaAl(OH)_4$ solutions of total constant stoichiometric ionic strength ranging from 1 to 6 mol kg^{-1} were prepared by mass.

Heat Capacity Measurements. The relative volumetric heat capacity differences ($\Delta\sigma/\sigma^R = (\sigma - \sigma^R)/\sigma^R$) between the test liquids and a reference (designated with a superscript R) were measured using a Picker flow calorimeter (Sodev, Sherbrooke, Canada) and the procedures described previously.[7]

To avoid precipitation of $Al(OH)_3$ in the calorimeter, which would occur if the concentrated aluminate solutions were measured directly against (i.e., displaced from the

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Table 1. Literature Data for the Heat Capacities of Alkaline Aluminate Solutions ($m^\circ = 1$ mol kg^{-1})

ref	t[a]/°C	$[\mathrm{NaOH}]_T$[a]/m°	$[\mathrm{Al(III)}]_T$[a]/m°	OH/Al[b]	comments
2	25−90	0.8−6.9[c]	0.1−3.4[c]	1.3−2.5	static calorimetry $\delta C_p \pm 0.5\%$
3	150−300	0.8−5.1[c]	0.1−3.1[c]	1.5−15	static calorimetry $\delta C_p \pm 0.5\%$
4	10−55	0.2−2.3	0.1−1.2	2 and 3	flow calorimetry $\delta C_p \pm 2$ mJ g^{-1} K^{-1}
5	50−250	0.2−1.2	0.1−0.5	~2.5	flow calorimetry; $P = 2.5{-}4.7$ MPa; $\delta C_p \pm 2$ mJ g^{-1} K^{-1} ($\delta C_{p\phi}^{\infty} \pm 10$ J K^{-1} mol^{-1})
6	100−150	0.3−4.9[d]	0.1−3.6[d]	0.4−22	reaction calorimetry + literature data

[a] Approximate values; note that $[\mathrm{NaOH}]_T$ refers to the total hydroxide in excess after the formation of $\mathrm{Al(OH)_4^-}$. [b] Ratio $[\mathrm{NaOH}]_T/[\mathrm{Al(III)}]_T$. [c] Converted from original mass % units. [d] Measured at $I/m^\circ = 1$, 3, and 5.

Table 2. Experimental Relative Volumetric Heat Capacities, $\Delta\sigma/\sigma^R$, Heat Capacities, C_p, and Mean Apparent Molar Heat Capacities, $C_{p\phi}$, of Aqueous Solutions of Sodium Hydroxide/Sodium Aluminate Mixtures at 25.0 °C and Total Stoichiometric Ionic Strengths I_T from 1 to 6 mol kg^{-1}

I_T/(mol kg^{-1})	$[\mathrm{Al(III)}]_T$/(mol kg^{-1})	mol % $\mathrm{Al(OH)_4^-}$ [a]	n[b]	$10^3\Delta\sigma/\sigma^R$ [c]	ρ[d]/(g cm^{-3})	C_p/(J K^{-1} g^{-1})	$C_{p\phi}$/(J K^{-1} mol^{-1})
$I = 1$ mol kg^{-1}							
1.0003	0.0000	0.00	3	−7.261(74)	1.039 27	3.982 88(30)	−39.66(31)
0.9989	0.1004	10.05	3	0.903(45)	1.042 44	3.975 71(18)	−16.24(19)
0.9963	0.1999	20.06	3	1.835(18)	1.045 15	3.968 94(7)	7.09(7)
1.0002	0.2997	29.96	3	2.769(10)	1.048 13	3.961 20(4)	30.33(4)
0.9981	0.4003	40.11	3	3.655(32)	1.050 89	3.954 13(13)	53.61(14)
1.0052	0.5005	49.79	3	4.574(18)	1.054 00	3.945 94(7)	76.28(8)
0.9942	0.5996	60.31	3	5.465(17)	1.056 38	3.940 39(7)	99.99(7)
1.00	1.00	100					192.4[e]
$I = 2$ mol kg^{-1}							
2.0061	0.0000	0.00	4	−2.298(32)	1.078 36	3.857 70(12)	−7.31(7)
1.9964	0.2004	10.04	2	1.889(19)	1.083 05	3.848 26(7)	16.92(4)
1.9998	0.4001	20.01	3	3.912(22)	1.088 21	3.837 74(9)	41.27(5)
2.0037	0.5998	29.93	2	5.874(6)	1.093 38	3.827 04(2)	65.30(1)
2.0041	0.7995	39.89	2	7.758(26)	1.098 43	3.816 59(10)	89.09(6)
1.9923	0.9982	50.10	2	9.549(39)	1.103 03	3.807 42(15)	113.07(8)
1.9977	1.1998	60.06	2	11.359(20)	1.108 30	3.796 11(7)	136.49(4)
2.00	2.00	100					232.8[e]
$I = 3$ mol kg^{-1}							
2.9981	0.0000	0.00	4	8.774(27)	1.114 20	3.775 02(10)	15.28(4)
2.9980	0.3003	10.02	2	2.888(35)	1.120 93	3.763 18(13)	40.24(5)
2.9997	0.6001	20.01	2	5.746(34)	1.127 71	3.751 22(13)	64.98(5)
3.0021	0.8993	29.96	2	8.441(31)	1.134 49	3.738 79(12)	89.27(5)
2.9987	1.1994	40.00	2	11.017(40)	1.141 10	3.726 60(15)	113.45(6)
3.0028	1.4985	49.90	2	13.524(102)	1.147 94	3.713 61(37)	137.09(15)
2.9981	1.7992	60.01	2	15.906(42)	1.154 56	3.700 98(15)	160.80(6)
3.00	3.00	100					258.6[e]
$I = 4$ mol kg^{-1}							
4.0020	0.0000	0.00	3	23.199(92)	1.147 98	3.716 34(33)	32.31(10)
4.0004	0.3998	9.99	2	3.435(63)	1.155 94	3.703 37(23)	57.36(7)
3.9993	0.7996	19.99	2	6.728(8)	1.163 93	3.690 04(3)	82.13(1)
3.9978	1.1999	30.01	3	9.811(65)	1.171 91	3.676 13(24)	106.56(7)
3.9968	1.5999	40.03	2	12.704(33)	1.179 90	3.661 68(12)	130.59(4)
3.9972	1.9995	50.02	2	15.533(43)	1.187 93	3.647 10(15)	154.34(5)
3.9989	2.3997	60.01	2	18.190(65)	1.196 01	3.631 96(23)	177.69(8)
4.00	4.00	100					275.4[e]
$I = 5$ mol kg^{-1}							
5.0065	0.0000	0.00	4	39.470(79)	1.179 49	3.674 57(28)	45.64(7)
5.0097	0.4997	9.97	2	3.603(6)	1.188 59	3.659 60(2)	70.58(1)
5.0108	1.0002	19.96	2	6.982(10)	1.197 64	3.644 17(4)	95.16(1)
5.0011	1.4991	29.98	2	9.948(17)	1.206 36	3.628 48(6)	119.28(2)
5.0041	1.9992	39.95	2	12.709(41)	1.215 46	3.611 17(15)	142.88(4)
5.0006	2.4998	49.99	2	15.534(30)	1.224 40	3.595 30(11)	166.39(3)
5.00	5.00	100					287.8[e]
$I = 6$ mol kg^{-1}							
6.0026	0.0000	0.00	3	56.073(61)	1.208 73	3.642 96(21)	55.92(4)
6.0031	0.5999	9.99	3	3.246(83)	1.218 51	3.625 50(30)	80.57(6)
6.0026	1.1995	19.98	2	6.217(28)	1.228 26	3.607 38(10)	104.78(2)
6.0014	1.7992	29.98	2	8.904(51)	1.237 99	3.588 58(18)	128.56(4)
5.9985	2.3996	40.00	2	11.441(42)	1.247 69	3.569 62(15)	152.05(3)
5.9994	2.9993	49.99	3	13.851(67)	1.257 48	3.550 28(24)	175.12(6)
6.00	6.00	100					294.9[e]

[a] Substitution of $\mathrm{OH^-}$. [b] n = number of independent measurements. [c] Values in parentheses are standard deviations in the last significant figure. [d] Interpolated from ref 11. [e] Extrapolated, hypothetical value for $\mathrm{NaAl(OH)_4(aq)}$.

calorimeter by) water, all aluminate solutions were measured against NaOH(aq) solutions of the same I as that of the reference. The required heat capacities for NaOH(aq) were taken from a previous publication[7] and were measured against water in the usual way in the same calorimeter under conditions similar to those of the present study. The daily operation of the calorimeter was checked by initial and final measurements of the reference NaOH(aq) solution against water. The heat capacities obtained always agreed with those of our previous study[7] to within the limits of the reproducibility of the calorimeter (±0.025%).

For reasons discussed in detail previously,[7] the reported heat capacities were determined from measurements in which NaOH(aq) was being displaced from the calorimeter by NaOH/NaAl(OH)$_4$(aq) (the first measurement "leg"). The accuracy of the NaOH(aq) data is discussed in detail elsewhere;[7] however, measurement against NaOH(aq), rather than the more accurately known water, inevitably means a loss of certainty in the heat capacities of the NaOH/NaAl(OH)$_4$ mixtures, due to error propagation. Previous detailed measurements using Na$_2$SO$_4$(aq) suggest that this effect is quite small for first "leg" measurements.[7] Thus, an overall uncertainty of about ±0.04% is estimated for the heat capacities of the NaOH/NaAl(OH)$_4$ solutions.

Heat capacities per unit mass (C_p/(J K^{-1} g^{-1})) of the target solutions were calculated from the measured volumetric heat capacities, using the expression

$$C_p = C_p^{\,R}\rho^R(1 + \Delta\sigma/\sigma^R)/\rho \qquad (2)$$

where the reference heat capacity ($C_p^{\,R}$/(J K^{-1} g^{-1})) and the reference and test solution densities (ρ^R, ρ/(g cm^{-3})) were taken from the literature[7,11] (see Table 2).

For the ternary NaOH/NaAl(OH)$_4$(aq) solutions, the mean apparent molar heat capacity, $C_{p\phi}$(mean), was calculated from the expression

$$C_{p\phi}(\text{mean}) = [C_p(1000 + m_2M_2 + m_3M_3) - 1000C_p^{\circ}]/(m_2 + m_3) \qquad (3)$$

where m and M are the molality and molar mass of the solutes, and the subscripts 2 and 3 denote NaOH and NaAl(OH)$_4$, respectively (by convention, 1 is the solvent). The density (ρ°) and heat capacity (C_p°) of pure water were taken as 0.997 047 g cm^{-3} and 4.1819 J K^{-1} g^{-1}, respectively,[12] as discussed elsewhere.[7]

As pure (neat) NaAl(OH)$_4$(aq) solutions are unstable, because of the sparing solubility of gibbsite at low hydroxide concentrations (see eq 1), their apparent molar heat capacities, $C_{p\phi3}$, were calculated from Young's rule,[4] which for this system can be written

$$C_{p\phi}(\text{mean}) = (m_2/I)C_{p\phi2} + (m_3/I)C_{p\phi3} \qquad (4)$$

Results and Discussion

The results obtained for alkaline sodium aluminate solutions at $1 \le I/\text{mol kg}^{-1} \le 6$ and with Al(OH)$_4^-$ substituting up to 60 mol % of the OH$^-$ in each constant I series are given in Table 2. The mean apparent molar heat capacities of the mixtures are also plotted in Figure 1, which shows that there is a close linear relationship ($R^2 \ge 0.9998$) between $C_{p\phi}$(mean) and the level of substitution of OH$^-$ by Al(OH)$_4^-$. In other words, the apparent molar heat capacities of these mixtures closely follow Young's rule (eq 4). It is noteworthy that the slopes of the lines in Figure 1 are virtually independent of I. This behavior may be contrasted with that observed previously for densities (or apparent molar volumes). The latter also closely follow Young's rule,[11] but the slopes of the plots of the ρ (or V_ϕ) versus mol % substitution increase with increasing I.

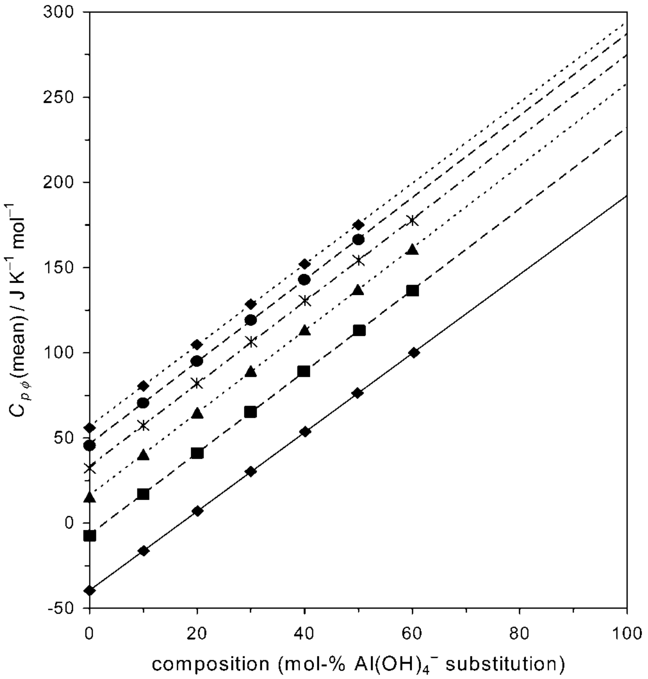

Figure 1. Mean apparent molar heat capacities of NaOH/NaAl(OH)$_4$ mixtures at 25 °C. The results are correlated by linear regression ($R^2 \ge 0.9998$): ◆, solid line, $I = 1$ mol kg^{-1}, $y = 2.319x - 39.47$; ■, dashed line, $I = 2$ mol kg^{-1}, $y = 2.397x - 6.94$; ▲, dotted line, $I = 3$ mol kg^{-1}, $y = 2.426x + 15.99$; ∗, dash−dot line, $I = 4$ mol kg^{-1}, $y = 2.422x + 33.17$; ●, dashed line, $I = 5$ mol kg^{-1}, $y = 2.414x + 46.36$; ◆, dotted line, $I = 6$ mol kg^{-1}, $y = 2.383x + 56.60$.

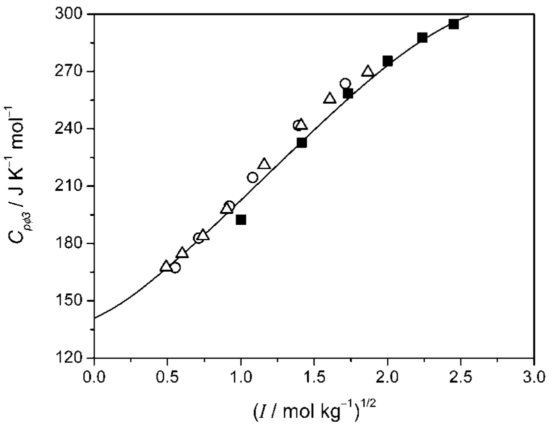

Figure 2. Apparent molar heat capacities of hypothetical pure NaAl(OH)$_4$(aq) solutions at 25 °C. Experimental data: ■, this work, ○, Hovey et al.,[4] 25 mol % aluminate substitution; △, Hovey et al.,[4] 33 mol % aluminate substitution. Calculated values: solid line, results of the Pitzer model described in the text.

The linearity of the plots in Figure 1 enables reasonably reliable estimates of the apparent molar heat capacities of the hypothetical pure NaAl(OH)$_4$(aq) solutions to be made by extrapolation. The results so obtained are plotted in Figure 2 together with the values of Hovey et al.,[4] which were derived from eq 4 using apparent molar heat capacities of NaOH(aq) calculated from the model of Simonson et al.[13] Also shown in Figure 2 are the $C_{p\phi3}$ values calculated using a Pitzer model that is based on that proposed by Wesolowski,[14] combined (this work) with the standard partial molar heat capacity of NaAl(OH)$_4$(aq) given by Hovey et al.[4] The practically ionic-strength-independent slopes obtained by linear regression of the observed heat capacities as a function of the degree of substitution of OH^- by $Al(OH)_4^-$ (Figure 1) indicate that Wesolowski's assumption of constant (i.e. temperature independent) differences between the Pitzer parameters of NaOH and $NaAl(OH)_4$ is reasonable. Therefore, the calculated line in Figure 2 has the same curvature as the apparent molar heat capacity function for NaOH(aq) and is only shifted by a constant value. The Pitzer equations for heat capacities are given in our previous paper,[7] and further details of the present model will be published elsewhere.[15]

The linearity of the heat capacities of $NaOH/NaAl(OH)_4$ solutions with composition (Figure 1) provides a sound basis for the prediction of the heat capacities of alkaline aluminate solutions under other conditions and in the presence of other dissolved species. The extent to which Young's rule is followed for other electrolyte mixtures of relevance to the Bayer process is currently being investigated.

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