Spectroscopic studies of the chemical speciation in concentrated alkaline aluminate solutions

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The [205]Tl NMR and UV/VIS spectral changes associated with the hydrolysis of thallium(I) have been employed to investigate hydroxide-sensitive equilibria in highly concentrated alkaline aluminate solutions {0.1 M < $[Al(III)]_T$ < 2.6 M; 0.15 M < $[NaOH]_T$ < 4.0 M} in an ionic medium of 8 M $Na(ClO_4)$ at 25 °C. Spectroscopic titrations were performed at $[OH^-]_T/[Al(III)]_T$ ratios of 6.08, 5.06, 4.59 and 4.33 and also at notionally constant $[OH^-]$. The data obtained demonstrate conclusively that the hydroxide concentration at high $[OH^-]_T$ and $[Al(III)]_T/[OH^-]_T$ ratios is significantly higher than if only the well established $Al(OH)_4^-$(aq) ion is present. In agreement with previous potentiometric results, the data are consistent with the formation of one or more oligomeric species of general formula $Al_q(OH)_{3q-r}^{r+}$(aq) (with $q = 4$–7 and $q + r = 1$ or 2). Evidence is also presented for the formation of at least one Tl(I)–aluminate solution species. However, unequivocal interpretation of the data is difficult because of possible ion pairing, solvation and activity coefficient effects occurring in these extremely concentrated electrolyte solutions.

Introduction

The recovery of purified alumina trihydrate [Gibbsite, $Al(OH)_3$-(s)] from bauxitic ores *via* the well known Bayer method is arguably the most economically significant of all hydrometal-lurgical processes. It is surprising therefore that, despite having been studied for over one hundred years, much of the detailed chemistry of the Bayer process remains poorly understood.[1,2] In particular, there is considerable uncertainty as to which species, other than the well characterized $Al(OH)_4^-$(aq) ion,[3–6] exist in Bayer "liquors" under industrial conditions. Since such species may provide a key to understanding critical aspects of the Bayer process, such as the slow precipitation kinetics, quantification of the chemical speciation in the concentrated alkaline aluminate solutions typical of Bayer liquors is of considerable interest.

Recently, hydrogen electrode potentiometry was used by us to monitor hydroxide concentrations up to 2 M in concentrated alkaline aluminate solutions in 8 M $Na(ClO_4)$ media.[7] The data obtained showed that $[OH^-]$ was significantly higher than if the only aluminium-containing species present was $Al(OH)_4^-$(aq). The results were consistent with the presence of one or more "hydroxide-deficient" polynuclear aluminate species whose formation can be represented by eqn. (1). [Note that this is a

$$qAl(OH)_3^0 + rH^+ \rightleftharpoons Al_q(OH)_{3q-r}^{r+} \qquad (1)$$
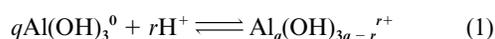
mathematical formalism and does not imply the significant formation of $Al(OH)_3^0$(aq) in solution; see ref. 7 for a full discussion.] However, on account of strong correlations in the data and possible ion-pairing effects, a definitive stoichiometry for these species could not be determined, establishing a need for further evidence.[7,8]

After potentiometry, spectroscopic methods are probably the best available for quantitative study of chemical speciation. Unfortunately, pure Al(III)/OH$^-$ solutions do not absorb[9] in the UV/VIS region, ^{27}Al NMR spectroscopy exhibits only a single broad resonance at *ca.* δ 80 [relative to $Al(H_2O)_6^{3+}$(aq)] which

appears to be virtually independent of both $[Al(III)]_T$ and $[OH^-]_T$,[10,11] and the vibrational spectroscopies are generally not sufficiently sensitive.[11] Thus, direct spectroscopic investigation of complex formation in concentrated alkaline aluminate solutions appears unpromising.

Recently it has been shown that the weak interaction between Tl(I) and OH$^-$ in aqueous solution can be followed both by UV/VIS and [205]Tl NMR spectroscopy.[12] As this interaction [to form $TlOH^0$(aq) and, to a much lesser extent, $Tl(OH)_2^-$(aq)][12] is significant only at very high pH ($[OH^-] \geqslant 0.1$ M), it is potentially suitable for the investigation of hydroxide-sensitive equilibria in concentrated alkaline aluminate solutions. The sensitivity of both spectroscopic techniques is reasonable: significant changes occur at 230–270 nm in the electronic spectrum and the [205]Tl NMR chemical shift changes by hundreds of ppm.

The use of this simple inorganic chromophore is appealing for a number of reasons. First, its chemical stability with respect to OH$^-$ avoids the problems which would be likely to occur with the use of conventional organic dyes. Furthermore, Tl(I) systems are labile, highly reversible, soluble and relatively non-complexing (at least towards typical "hard" species).

Thus, this paper presents a detailed investigation, using Tl(I) as a probe, of hydroxide-sensitive equilibria in concentrated alkaline aluminate solutions at industrially-relevant compositions identical to those employed in our previous potentiometric study.[7] The changes in the speciation of Tl(I) are followed both by UV/VIS and [205]Tl NMR spectroscopy, as previously described for the binary Tl(I)/OH$^-$ system.[12]

Experimental

Materials

All solutions were prepared from high purity water (Millipore Milli-Q system). Analytical grade $NaClO_4 \cdot xH_2O$ (Aldrich, USA, "99.99%" grade) was recrystallized three times from water. The water content of the resulting solid was then determined by thermogravimetric analysis. Thallium(I) perchlorate

stock solutions were prepared from Tl_2CO_3 (Sigma, "99.999%" grade) as described elsewhere [12] and all the usual precautions for dealing with Tl(I) solutions were followed.[12]

Stock solutions of hydroxide (*ca.* 8 M) were prepared from NaOH (Ajax Chemicals, Australia, analytical grade, 98 mol %). The carbonate content of the base solutions was minimized by addition of CaO(s) to the stock solution and subsequent filtration.[13] Solutions were analysed and standardized pH-metrically [14] and were found to have a carbonate concentration less than 0.05% of the total alkalinity (*i.e.* < 4 mM in 8 M NaOH solution).

Sodium aluminate solutions were prepared by quantitative dissolution of high purity Al wire (Goodfellow, UK, "99.999%" grade) in *ca.* 8 M NaOH.[7] The $[OH^-]_T/[Al(III)]_T$ ratios in these solutions were 6.08, 5.06, 4.59 and 4.33, corresponding to aluminium concentrations of 2.663, 3.826, 5.152 and 6.224 M, respectively.

Prior to the experiments, all solutions were filtered on a supported membrane (0.45 μm) equipped with a carbon dioxide trap.

Overall approach

Two types of experiments were performed with each spectroscopic technique. In the first type, $[OH^-]_T/[Al(III)]_T$, which can be defined as in eqn. (2) where the subscript T denotes analytical or total concentration, was held constant and $[NaOH]_T$ and $[Al(III)]_T$ were changed in parallel. In the second type, the notional free hydroxide ion concentration, $[OH^-]_N$, defined as in eqn. (3) was held constant and $[Al(III)]_T$ varied.

$$[OH^-]_T/[Al(III)]_T = \{[NaOH]_T + 3 [Al(III)]_T\}/[Al(III)]_T \quad (2)$$

analytical or total concentration, was held constant and $[NaOH]_T$ and $[Al(III)]_T$ were changed in parallel. In the second type, the notional free hydroxide ion concentration, $[OH^-]_N$, defined as in eqn. (3) was held constant and $[Al(III)]_T$ varied.

$$[OH^-]_N = [NaOH]_T - [Al(III)]_T \quad (3)$$

Note that $[OH^-]_N$ is the actual free hydroxide ion concentration if the only significant aluminium-containing complex in solution is $Al(OH)_4^-$(aq), *i.e.* each Al(III) binds exactly four OH^-. All measurements were made at 25 °C (±1 °C for the NMR, ±0.05 °C for the UV/VIS spectroscopy) in an 8 M $Na(ClO_4)$ ionic medium.

^{205}Tl NMR spectroscopy

The ^{205}Tl NMR spectra were recorded using 200–1000 transients, 2048 points and a 2–10 kHz spectral width on a Bruker AC 200 spectrometer equipped with a normal broad band probe head operating at 360 MHz so that the ^{205}Tl observation frequency was 115.4 MHz. No lock could be used and measurements were performed in the sweep-off mode. Field homogeneity was maintained by shimming the FID/lineshape of a concentrated $TlClO_4$ stock solution [0.080 M, $I = 8$ M $Na(ClO_4)$, pH 6–8]. The reproducibility of these measurements on randomly-duplicated samples was within 5 ppm.

Five series of samples were prepared each consisting of 9–12 solutions. The $[Tl(I)]_T$ was held constant at 0.040 M as the ^{205}Tl NMR chemical shift depends on the metal concentration.[15] Three series were at constant $[OH^-]_T/[Al(III)]_T$ (6.08, 5.06 and 4.59 respectively) with 0.1 M $\leq [Al(III)]_T \leq 2.6$ M. Within the constant $[OH^-]_N$ series $[Al(III)]_T$ varied from 0 to 1.63 M and $[OH^-]_N$ was 1.00 and 2.00 M, respectively. The ^{205}Tl NMR data were evaluated using the computer program PSEQUAD.[16]

UV/VIS spectrophotometry

The UV/VIS absorption spectra were measured with a Hewlett-Packard 8452A diode array spectrophotometer. A special combined potentiometric-spectrophotometric tall-form water-jacketed titration cell with a path length of 0.909 mm[17] was constructed from Pyrex glass with quartz windows joined by appropriate graded seals. The temperature in the cell was main-

tained at 25.0 ± 0.05 °C by use of a refrigerated circulator-thermostat (Heto Model 04 PT 623).

The spectra were recorded against water over the wavelength range 230–360 nm.[12] However, only the data points between 234 and 280 nm were used for evaluation because of interference from the strong UV band of the hydroxide ion at $\lambda < 230$ nm[9] and the absence of significant absorbance at $\lambda > 300$ nm. The spectroscopic purity of the base, background electrolyte and aluminate solutions were always checked.[9] Only solutions contributing less than 0.01 to the absorbance at $\lambda \geqslant 234$ nm were utilized. Absorbances of the duplicate runs were reproducible to better than 0.01.

Experiments at constant $[OH^-]_T/[Al(III)]_T$ involved titration of 40.00 mL of a solution of $[TlClO_4]_T = 0.010\ 04$ M, $I = 8$ M $(Na)ClO_4$, pH 6–8 with an alkaline aluminate solution. The concentration of $[Al(III)]_T$ in the titrant solutions was 4.03, 5.15 and 6.22 M, corresponding to $[OH^-]_T/[Al(III)]_T = 4.985$, 4.614 and 4.338, respectively, and $[NaOH]_T$ was *ca.* 8 M but accurately known. Each titration involved 20–30 additions and $[Al(III)]_T$ in the test solution varied from 0 to 2.45 M. During the constant $[OH^-]_N$ experiments, an accurately known volume (45.83 mL) of a solution of $[TlClO_4]_T = 0.008\ 766$ M, $[NaOH]_T = 1.000$ M, $I = 8$ M $(NaClO_4)$ was placed in the titration cell. The titrant solution was $[NaOH]_T = 4.271$ M, $[Al(III)]_T = 3.269$ M, $I = 8$ M $Na(ClO_4)$. The $[Al(III)]_T$ in the cell varied from 0.05 to 2.45 M in the course of the titration. This arrangement meant that $[OH^-]_N$ was exactly 1.00 M.

Titrant solutions were delivered into the cell from a calibrated Metrohm 665 Dosimat automatic burette. After each addition, the system was allowed to equilibrate for at least 5 min prior to recording the spectrum. The experiments were designed in such a way that the majority (>90%) of the absorbance readings fell in the range where the signal-to-noise ratio is optimal ($0.2 \leqslant A \leqslant 1$). The UV/VIS data were analysed using the SPECFIT[18] global optimizing software.

Light scattering measurements were performed on a Brice-Phoenix Universal LS Photometer.

Results

^{205}Tl NMR spectroscopy

All ^{205}Tl NMR spectra exhibited a single peak over the entire hydroxide and aluminium concentration ranges studied. This indicates that the chemical exchange between any Tl(I) complexes present is fast on the NMR time scale. The peak is shifted upfield from Tl^+(aq) by several hundred ppm with increasing $[NaOH]_T$ and $[Al(III)]_T$ concentrations and hydroxide-to-aluminium ratio (Fig. 1).

The dotted lines in Fig. 1 represent the chemical shifts calculated assuming that $Al(OH)_4^-$(aq) is the only aluminium-containing species in solution and that the chemical shift of Tl(I) depends only upon the free $[OH^-]$, *i.e.* there is no interaction between Tl(I) and $Al(OH)_4^-$(aq). Quite clearly, the observed chemical shifts are systematically higher than the calculated values with the difference increasing as the hydroxide-to-aluminium ratio decreases.
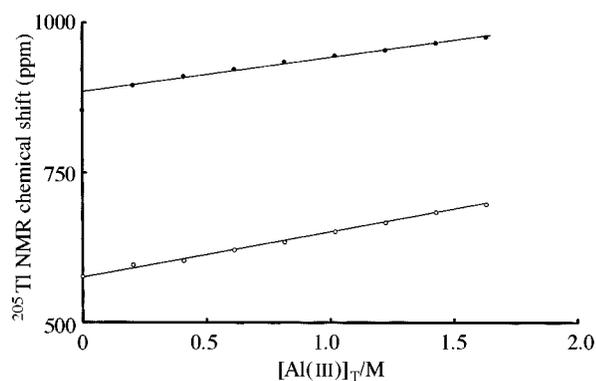
To extend the experimental data, two series of solutions with constant $[OH^-]_N$ (1.00 and 2.00 M) were investigated. Within each series $[Al(III)]_T$ was varied between 0 and 1.633 M at constant ionic strength [8 M $Na(ClO_4)$]. If the above assumptions were correct, then the actual $[OH^-]$ and hence the chemical shift would have been constant. Fig. 2 shows that this is not the case as the observed chemical shift increases with the increasing $[Al(III)]_T$. This result is consistent with the data in Fig. 1 and strongly indicates the existence of other species in the system.

UV/VIS Spectrophotometry

When a $TlClO_4/NaClO_4$ mixture was titrated with an alkaline aluminate solution at constant $[OH^-]_T/[Al(III)]_T$, a broad
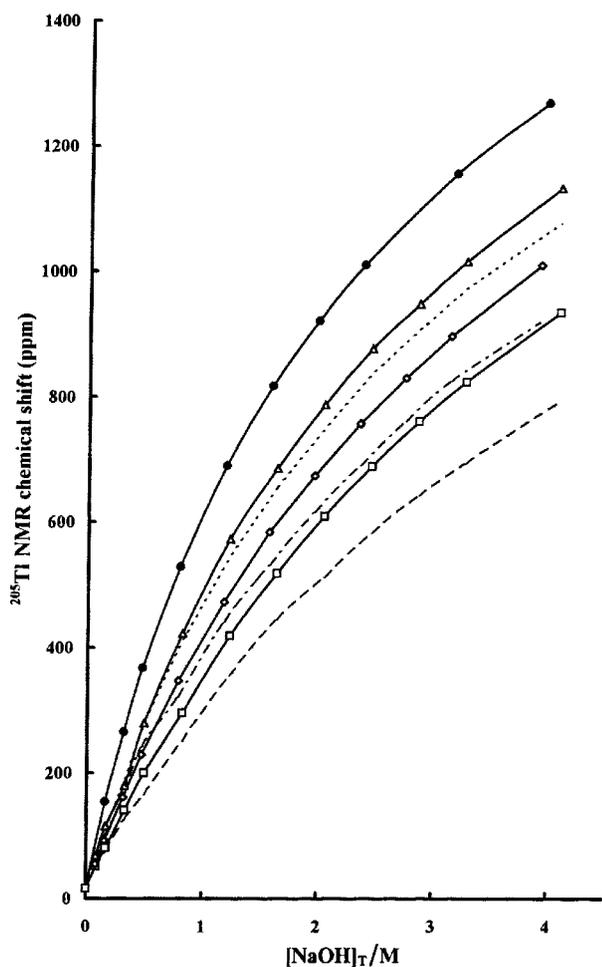
Fig. 1 Variation of ^{205}Tl NMR chemical shift with $[NaOH]_T$ at different $[OH^-]_T/[Al(III)]_T$ ratios. ●: Al(III)-free system; Δ: $[OH^-]_T/[Al(III)]_T = 6.08$, ◇: $[OH^-]_T/[Al(III)]_T = 5.06$, □: $[OH^-]_T/[Al(III)]_T = 4.59$. The dotted lines are calculated assuming $Al(OH)_4^-$(aq) is the only Al(III)-containing species present.


Fig. 2 Variation of ^{205}Tl NMR chemical shift with $[Al(III)]_T$ at various $[OH^-]_N$. ○: 1.00; 1 ●: 2.00 M.

Fig. 3 Typical UV spectra, corrected for dilution, $[Tl(I)] = 0.010\ 04$ M titrated with a solution of $[OH^-]_T/[Al(III)]_T = 4.614$, with $[Al(III)]_T$ from bottom to top: 0, 0.245, 0.468, 0.767, 1.189, 1.599, 2.030 M. Inset: spectra obtained under identical conditions at $[Al(III)]_T = 0$ M. The free hydroxide ion concentrations in these measurements are roughly the same as those in the main figure.
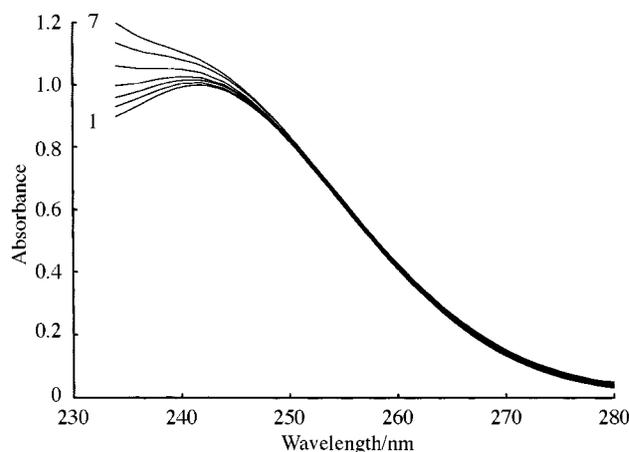
Fig. 4 The UV spectra (corrected for dilution) obtained at $[Tl(I)]_T = 0.010\ 04$ M and $[OH^-]_N = 1.00$ M at $I = 8$ M (NaClO$_4$); $[Al(III)]_T$ varies from 0 (spectrum 1) to 1.453 M (spectrum 7).

$[Al(III)]_T$. Experiments at constant $[OH^-]_N$ confirmed the presence of this new band (Fig. 4).

Several experiments were performed to clarify the origin of this new band and to rule out artefacts. First, the spectroscopic purity of all solutions was checked. Only reagents with absorbances of less than 0.01 in the relevant wavelength range were used, excluding the possibility that the observed effects might stem from impurities.

Secondly, possible chromogenic interactions between individually "colourless" components were investigated. The spectra of 1:1 (v/v) mixtures of: (i) 8 M NaClO$_4$ with 8 M NaOH; (ii) 8 M NaClO$_4$ solution containing 8 M NaOH and 6.265 M Al(OH)$_3$ were recorded. No spectral changes were observed for these solutions or their mixtures indicating that the absorbance at $\lambda < 250$ nm in Figs. 3 and 4 cannot be associated with interactions between ClO$_4^-$ and OH$^-$ or ClO$_4^-$ and Al(III).

Finally, to detect possible micro-inhomogeneities, which might contribute to the absorbance of the solutions at short wavelengths, the static light scattering properties of (i) 8 M NaClO$_4$; (ii) 8 M NaClO$_4$/0.01 M TlClO$_4$; (iii) 4.65 M NaOH/2.88 M Al(OH)$_3$ solution and their 1:1 mixtures were measured. All gave dissymmetry ratios close to unity (1.00 ± 0.05), indicating clean, particulate-free solutions with no significant presence of particles >20 nm.

Thus, it may be concluded that the increase in absorbance at $\lambda < 250$ nm is related to the formation of at least one new species, formed *via* an interaction between Tl(I) and Al(III)-

shoulder appeared at 230 nm $< \lambda < 280$ nm. The absorbance increased with increasing $[NaOH]_T$. This is illustrated in Fig. 3 which also includes some spectra of Al(III)-free solutions at approximately the same $[OH^-]_N$. As $[OH^-]_T$ increases, a well defined absorption maximum associated with the formation of TlOH^0(aq) and Tl(OH)$_2^-$(aq)[12] appears around 240 nm in the Al(III)-free system.

In the presence of Al(III), however, the maximum at 240 nm virtually disappears and the tail of a new spectral band presents itself at $\lambda < 250$ nm. When the spectra are recorded at different $[OH^-]_T/[Al(III)]_T$ (not shown), it becomes evident that the intensity of the new band is inversely proportional to $[OH^-]_T/$

containing species. Recent [19] ^{27}Al NMR measurements qualitatively support this statement: in a solution containing 0.27 M Al(III) and 0.44 M NaOH at $I = 8$ M (NaClO$_4$) the ^{27}Al NMR resonance peak at *ca.* δ 80 broadens considerably (*ca.* 20%) when a relatively minor amount of Tl(I) (0.050 M) is added to the system.

Discussion

Thallium(I) is similar in various respects to alkali metal cations such as Na$^+$ and K$^+$.[20] Comparison of the standard formation constants of the related MOH^0(aq) ion pairs, K^0_M [corresponding to the equilibria M$^+$(aq) + OH$^-$ (aq) $\rightleftharpoons$ MOH^0(aq)] suggests that Tl(I) may form slightly stronger complexes with simple inorganic species ($K^0_{Na} = 0.7 \pm 0.3$ M^{-1},[21] $K^0_K = 0.40 \pm 0.3$ M^{-1},[21] $K^0_{Tl} = 4.9$ M^{-1} [22]). It has also been established that Na$^+$ forms ion pairs with Al(OH)$_4$$^-$(aq)[23,24] implying a significant interaction between Tl$^+$(aq) and Al(OH)$_4$$^-$(aq). However, the large (*ca.* 800-fold) excess of Na$^+$ in the present measurements might suppress such species.
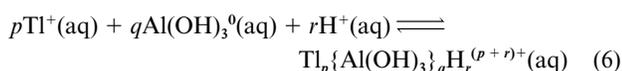
This interaction makes Tl(I) less than ideal since the spectroscopic changes associated with variations in [OH$^-$] will occur in parallel with the formation of the "thallium–aluminate" species. Interactions in aqueous Tl(I)/Al(III)/OH$^-$ systems have not been well characterized, although the preparation[25] and some spectral properties[26] of solid Tl$_2$[Al(OH)$_5$(H$_2$O)]·H$_2$O have been reported.

The formation constants and spectral characteristics of Tl$^+$(aq), TlOH^0(aq) and Tl(OH)$_2$$^-$(aq) which have been determined previously under identical experimental conditions (Table II and Fig. 3 in ref. 12) were held constant during the evaluation. The species Al(OH)$_3$^{0}(aq) was selected as a suitable basis against which all the speciation changes were postulated. [Note, as stated earlier, this does not imply that Al(OH)$_3$^{0}(aq) forms to any significant extent in these solutions. It is used only as a computational convenience; virtually identical results would be obtained if, say, Al^{3+}(aq) or Al(OH)$_4$$^-$(aq) were employed as the basis species.] The formation constant of Al(OH)$_4$$^-$(aq) is defined in terms of the basis species as shown in eqn. (4) for which eqn. (5) was held constant (log $\beta_{01-1} = -10.2$).[7]

$$\text{Al(OH)}_3{}^0\text{(aq)} + \text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_4{}^-\text{(aq)} + \text{H}^+\text{(aq)} \quad (4)$$

$$\beta_{01-1} = \frac{[\text{Al(OH)}_4{}^-\text{(aq)}]}{[\text{Al(OH)}_3{}^0\text{(aq)}]\,[\text{H}^+\text{(aq)}]^{-1}} \quad (5)$$

Spectra were analysed in terms of the equilibria (6) for which the formation constant β_{pqr} is defined as in eqn. (7).

$$p\text{Tl}^+\text{(aq)} + q\text{Al(OH)}_3{}^0\text{(aq)} + r\text{H}^+\text{(aq)} \rightleftharpoons$$
$$\text{Tl}_p\{\text{Al(OH)}_3\}_q\text{H}_r{}^{(p+r)+}\text{(aq)} \quad (6)$$

$$\beta_{pqr} = \frac{[\text{Tl}_p\{\text{Al(OH)}_3\}_q\text{H}_r{}^{(r+p)+}\text{(aq)}]}{[\text{Tl}^+\text{(aq)}]^p\,[\text{Al(OH)}_3{}^0\text{(aq)}]^q\,[\text{H}^+\text{(aq)}]^r} \quad (7)$$

Factor analysis[18] on the UV/VIS data indicated that the Tl(I)/Al(III)/OH$^-$ system has five, or possibly six, spectroscopically significant species, including Tl$^+$(aq), TlOH^0(aq) and Tl(OH)$_2$$^-$(aq).

The "interaction-free" model [Tl$^+$(aq), TlOH^0(aq), Tl(OH)$_2$$^-$(aq) and Al(OH)$_4$$^-$(aq), with fixed formation constants and spectra/chemical shifts] gave a poor overall fit. Inclusion of TlAl(OH)$_4$^{0}(aq) yielded a 40–70% improvement and the calculated formation constant (log $\beta_{11-1} = -10.95 \pm 0.15$) was virtually independent of the [OH$^-$]$_T$/[Al(III)]$_T$. Nevertheless, the overall fit was still about 10–20 times worse than acceptable; calculated spectra at different [OH$^-$]$_T$/[Al(III)]$_T$ showed systematic differences; standard deviations in the formation constants

were only fair (>0.1 log unit) and the program failed to converge in many cases.

Assuming that the absorbance at $\lambda > 250$ nm in the presence of Al(III) is due solely to TlOH^0(aq) and Tl(OH)$_2$$^-$(aq) (Fig. 4) then eqn. (8) applies where the asterisk denotes concentrations

$$[\text{TlOH}^0\text{(aq)}] + [\text{Tl(OH)}_2{}^-\text{(aq)}] =$$
$$[\text{TlOH}^0\text{(aq)}]^* + [\text{Tl(OH)}_2{}^-\text{(aq)}]^* \quad (8)$$

in the presence of Al(III). From this eqn. (9) can be derived

$$\frac{[\text{Tl}^+\text{(aq)}]}{[\text{Tl}^+\text{(aq)}]^*} = \frac{[\text{OH}^-\text{(aq)}]^*\,\{1 + K_2[\text{OH}^-\text{(aq)}]^*\}}{[\text{OH}^-\text{(aq)}]\,\{1 + K_2[\text{OH}^-\text{(aq)}]\}} \quad (9)$$

where K_2 is the stepwise formation constant of Tl(OH)$_2$$^-$(aq). This leads to eqn. (10) from which it is readily shown that

$$\text{TlOH}^0\text{(aq)} + \text{OH}^-\text{(aq)} \rightleftharpoons \text{Tl(OH)}_2{}^-\text{(aq)} \quad (10)$$
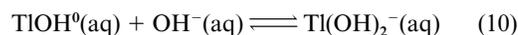
$[\text{OH}^-\text{(aq)}]^*\{1 + K_2[\text{OH}^-\text{(aq)}]^*\}/[\text{OH}^-\text{(aq)}]\{1 + K_2[\text{OH}^-\text{(aq)}]\}$ > 1 and therefore that $[\text{OH}^-\text{(aq)}]^* > [\text{OH}^-\text{(aq)}]$. In other words, the UV/VIS spectra can best be explained in terms of a greater concentration of free hydroxide in the aluminate-containing solutions than is calculated on the assumption that Al(OH)$_4$$^-$(aq) and TlAl(OH)$_4$^{0}(aq) are the only aluminium-containing species present. This argument fails only if the "thallium–aluminate" complex is formed to a very small extent and has an exceptionally high absorptivity.

Simulation of the observed ^{205}Tl NMR chemical shifts assuming only Tl(OH)$_n$$^{(1-n)+}$(aq) ($n = 0$–2) and TlAl(OH)$_4$^{0}(aq) were present yielded an unrealistic limiting chemical shift for TlAl(OH)$_4$^{0}(aq) (more than 100 000 ppm) with a small formation constant and large standard deviation. This failure might arise from strong correlation between the two optimized parameters log β_{11-1} and δ_{11-1}. Thus model calculations were performed keeping log β_{11-1} constant and optimizing δ_{11-1}. "Realistic" values were chosen for log β_{11-1}, *i.e.* which guaranteed that [TlAl(OH)$_4$^{0}(aq)] account for at least 10% of [Tl(I)]$_T$. As a result, the goodness of fit worsened significantly and the optimized values of δ_{11-1} were several thousand ppm. This is still far too high, since the ^{205}Tl NMR chemical shifts of inorganic Tl(I) salts in aqueous solutions span only a few hundred ppm [relative to Tl$^+$(aq) at infinite dilution] even when complexed with crown ethers.[27,28] Also, it is unlikely that δ_{11-1} [for TlAl(OH)$_4$^{0}(aq)] would be higher than δ_{10-1} [for Tl(OH)^0-(aq)] which is itself unusually large.[12] The more plausible explanation is the increased concentration of [OH$^-$] at high [OH$^-$]$_T$ and high [OH$^-$]$_T$/[Al(III)]$_T$ as argued in the previous section. Certainly, these calculations indicate that a model which includes just TlAl(OH)$_4$^{0}(aq) and the binary Tl(I)/OH$^-$ species does not satisfactorily account for the experimental results. Further species must be invoked.

As Al(III) species such as Al(OH)$_5$$^{2-}$(aq) or Al(OH)$_6$$^{3-}$(aq) would cause an effect opposite to that observed, their formation can be ruled out under these experimental conditions. As a next step, Al(III) species formed *via* hydroxide *release* from Al(OH)$_4$$^-$(aq) were considered. On the basis of our previous potentiometric studies,[7] the most likely species are those of general formula Al$_q$(OH)$_{3q-r}$$^{r+}$(aq) ($q = 4$–7, $q + r = 1$ or 2). Note, as discussed in detail elsewhere,[7] this does not mean that lower (or higher for that matter) Al–OH oligomers do not form but rather that their formation alone is not consistent with the observed spectral (and potentiometric[7]) effects in the accessible concentration range.

The ^{205}Tl NMR data could not be optimized simultaneously for Al$_q$(OH)$_{3q-r}$$^{r+}$(aq) and TlAl(OH)$_4$^{0}(aq). Optimizations of an Al(III) oligomer alone produced acceptable fits (Table 1) which were almost independent of the stoichiometry in accord with our potentiometric findings.[7] The log β_{0qr} values were

Table 1 Formation constants (log β_{0qr}), standard deviations (SD) and fitting parameters for $Al_q(OH)_{3q-r}^{r+}$ (aq) complexes calculated from ^{205}Tl NMR and UV/VIS data, $I = 8$ M (NaClO$_4$), 25 °C; log $\beta_{011} = 5.123$

| | Potentiometry | UV/VIS | | | ^{205}Tl NMR | |
0qr	log β_{0qr} (SD)[a]	log β_{0qr} (SD)[b]	Fit[c] (%)		log β_{0qr}[d]	Fit[e]
04−3	−11.7(06)	−11.7(10)	38		−9.2(12)	0.31
04−2	−25.8(07)	−25.9(07)	35		−25.0(06)	0.58
05−4	−35.4(10)	−35.4(13)	37		f	—
05−3	−17.0(06)	−17.0(08)	42		−15.7(08)	0.51
06−5	−45.1(14)	−45.1(18)	35		f	—
06−4	−31.27(07)	−31.1(08)	43		−29.0(12)	0.44
06−3	−17.0(06)	−16.9(08)	40		−15.9(09)	0.67
07−5	−41.0(08)	−40.7(12)	40		−37.4(16)	0.38

[a] Optimized values from ref. 7. [b] Calculated parameters at $[OH^-]_T/[Al(III)]_T = 4.985$ (entire data set). Formation constants and spectral parameters of Tl(I)/OH$^-$ species[12] and TlAl(OH)$_4^0$(aq) (log $\beta_{11-1} = -10.98 \pm 0.1$) held constant during optimization. [c] Improvement in fit (%) when $Al_q(OH)_{3q-r}^{r+}$(aq) is introduced into the model. [d] Calculated parameters from ^{205}Tl NMR data (entire data set) assuming no Tl(I)/Al(III) species. Formation constants and spectral parameters of Tl(I)/OH$^-$ species[12] held constant during optimization. [e] Fitting parameter. [f] Failure in optimization.
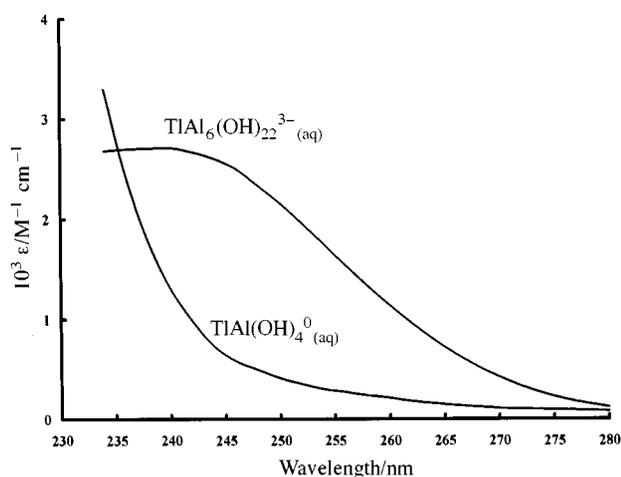
Fig. 5 Calculated absorptivities of TlAl(OH)$_4^0$(aq) and TlAl$_6$(OH)$_{22}^{3-}$ (aq) at 8 M (NaClO$_4$) ionic strength.

systematically higher than potentiometric values (Table 1) probably due to the presence of TlAl(OH)$_4^0$(aq).

Simultaneous optimization of the UV/VIS data using $Al_q(OH)_{3q-r}^{r+}$(aq) and TlAl(OH)$_4^0$(aq) also failed to converge. Since Al(III) oligomers are almost certainly non-absorbing,[9] they cannot account for the increased absorbance at $\lambda < 250$ nm. Thus the simplification used for the ^{205}Tl NMR data does not apply and inclusion of a Tl(I)–aluminate species becomes essential. The following strategy was therefore adopted. Aluminium(III) was assumed to exist exclusively as Al(OH)$_4^-$(aq) at low $[Al(III)]_T$ and high $[OH^-]_T$ concentrations.[7] In such solutions TlAl(OH)$_4^0$(aq) will be the only likely additional complex. Factor analysis on a truncated data set where only Al(OH)$_4^-$(aq) exists[7] indicated only four spectroscopically-significant complexes. This gave an acceptable spectrum (Fig. 5) and formation constant (log $\beta_{11-1} = -11.0 \pm 0.1$) for TlAl(OH)$_4^0$(aq).

Holding the spectrum of TlAl(OH)$_4^0$(aq) and log β_{11-1} constant, the formation constants of a range of Al(III) oligomers were then optimized, using the full UV/VIS data set (Table 1). The introduction of any one of the postulated[7] oligomeric species caused significant improvement in the fit (up to 45%). The calculated standard deviations were acceptable[7] and convergence was achieved for all $[OH^-]_T/[Al(III)]_T$

ratios and 0qr stoichiometries. As with the potentiometry,[7] the quality of the fit was independent of the chosen oligomer stoichiometry.

General comments and conclusions

The major conclusion which can be derived from these results is that there is an *increase* in $[OH^-]$ in alkaline aluminate solutions at high $[OH^-]_T$ and $[Al(III)]_T$. This apparent contradiction of Le Chatelier's principle is consistent with the formation of oligomers of general formula $Al_q(OH)_{3q-r}^{r+}$(aq) ($q = 4$–7, $q + r = 1$ or 2). However, because of the necessarily indirect and limited nature of the spectral information (both UV/VIS and ^{205}Tl NMR) obtainable and the correlation of errors, a precise stoichiometry cannot be derived. Even though there is gratifying agreement between the two spectroscopic techniques and the previous potentiometric investigations,[7] both as to the nature of the complexes and their formation constants, the proposed model must be regarded with some caution. The very high ionic strength and, more important, the high level of replacement of the ionic medium by the interacting species which was necessary to obtain significant effects at industrially-relevant compositions, meant that factors such as weak ion pairing [for example of Na$^+$ with OH$^-$ [21,23] or Al(OH)$_4^-$ [23,24]], or activity coefficient variations, may significantly influence the analysis.

Unfortunately, quantitative data for these effects, particularly in the present medium, are unavailable and are not easily estimated. It is worthwhile noting, however, that Raman spectra of solutions similar to those used in the present investigation[11,29] show clear evidence of species other than Al(OH)$_4^-$(aq). Whether these species are the same as those suggested by the present data cannot be determined at this stage. The poor sensitivity of Raman spectroscopy makes the necessary detailed investigation of the spectra with respect to aluminium concentration difficult.†,[29]

† *Note added at proof*: Since the submission of this paper, work by Buvári-Barcza *et al.*[30] has come to our attention. Their speciation conclusions based on viscosity and conductivity measurements imply a *decrease* in free $[OH^-]$ with increasing $[Al(III)]_T$ in direct contradiction to our present and previous[7] work. we have no specific explanation for this difference but note that their speciation results are technique-dependent, a problem shared with many of the earlier studies of this system.

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