The Ultraviolet Absorption Spectra of Synthetic Bayer Liquors

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Rigorously pure synthetic Bayer liquors are found to be entirely transparent in the UV–VIS range (down to 230 nm), contrary to reports by several groups whose spectra are shown to be due not to aluminate species but to trace contaminants in commercial aluminium samples, even of analytical grade.

The considerable commercial importance of the Bayer process for converting bauxite ore into alumina has ensured that it has been the subject of intensive research over many decades. Nevertheless, the nature of aluminate solutions has remained controversial from as early as 1913.[1,2] The problem is evident from the discordance between the major reviews published in this area by Misra,[3] Glastonbury,[4] Eremin and co-workers[5] and Zambo.[6] A plethora of species has been postulated but none except $Al(OH)_4^-$ is as yet very convincing.

Some recent reports regarding the UV–VIS spectra of these systems are of immediate interest. Such measurements have been employed by a number of researchers to investigate concentrated sodium aluminate solutions.[7–9] Unfortunately, the primary experimental observations and, consequently, the structural conclusions of these studies are in marked disagreement. Sato[7] has proposed that bands observed in synthetic Bayer liquors at *ca.* 230 and 265–270 nm are due to the formation of the species $Al(H_2O)_6^{3+}$ and $Al(OH)_4(H_2O)_2^-$, respectively. Dubrovinskii *et al.*,[8] however, reported a strong band at 230 nm in solutions containing only NaOH. From the low absorbances observed, these authors proposed that only a small proportion of the dissolved aluminium forms a UV-active complex (with λ_{max} at *ca.* 270 nm). Finally, Chen *et al.*[9] found a broad shoulder instead of a peak in the 230–280 nm region. The spectra were reported to be dependent on time and on the preparative history of the solutions and the authors concluded that a dimeric $[(OH)_3Al–O–Al(OH)_3]^{2-}$ was the absorbing species. This idea seemed to be supported by *ab initio* quantum chemical calculations and Raman spectroscopic measurements.[9]

Accordingly, the present work re-examines the UV spectra of synthetic Bayer liquors down to 230 nm. Special attention is paid to the purity of the chemicals used to prepare these highly concentrated solutions in view of the tendency of most species to absorb in the UV region and of the great sensitivity of UV spectrophotometry.

First, UV spectra of NaOH solutions in water were carefully recorded over the concentration range of 1–16 mol dm^{-3}. By using NaOH samples from different sources and of differing nominal grade, a broad weak shoulder between 230 and 300 nm was seen to be inversely correlated with sample purity. The variation in the absorbance with the concentration of NaOH obeyed the Lambert–Beer law but the apparent absorptivities at a given wavelength differed for samples from different suppliers. It is clear that at least some of the absorbance originates from trace amounts of UV-active contaminants in the solid NaOH reagent. As the BDH analytical grade NaOH exhibited a relatively low UV absorbance this was used in all subsequent preparations.

Table 1 Origin, purity and assay of aluminium samples

Sample	Source	Purity	Manufacturer's assay (in ppm)
A	Riedel-de Haën	99.0%	Fe: 2000, Cu: 200, Ti: 300 Zn: 800
B	Johnson Matthey	99.5%	Not available
C	Ajax	Technical	Not available
D	BDH	99.9%	Fe: 80, Mn: 20, Ti: 50, Cu: 50
E	Goodfellow	99.999%	Fe: <0.7, Mn: <0.2, Ni: <0.6, Ti: <0.3, Cu: 0.3

Sodium aluminate solutions were then prepared with various mole ratios of NaOH to $Al(OH)_3$ {[NaOH] = 1–16 mol dm^{-3}; $[Al(OH)_3]$ = 1–6 mol dm^{-3}} by dissolving aluminium metal in aqueous NaOH to achieve aluminium/caustic ratios typical of those for real Bayer liquors.[3] The origin, form and purity of the aluminium samples are detailed in Table 1. All digestions were carried out in loosely covered polyethylene or Pyrex glass vessels. No spectral differences were evident from samples digested in either apparatus.

After dissolution of the metal, the liquor was cooled in an ice bath, filtered on a supported Nalgene membrane filter (pore size 0.45 μm) and stored in closed polyethylene bottles. Spectra were recorded on a Hewlett-Packard 8452A spectrophotometer immediately following preparation, and again one week later. The solutions were stored at ambient temperature (23 ± 2 °C) in a thermostatted room. The optical measurements were made in 10 mm quartz cuvettes, with distilled water as the blank. All the water used in this work was deionized and distilled.

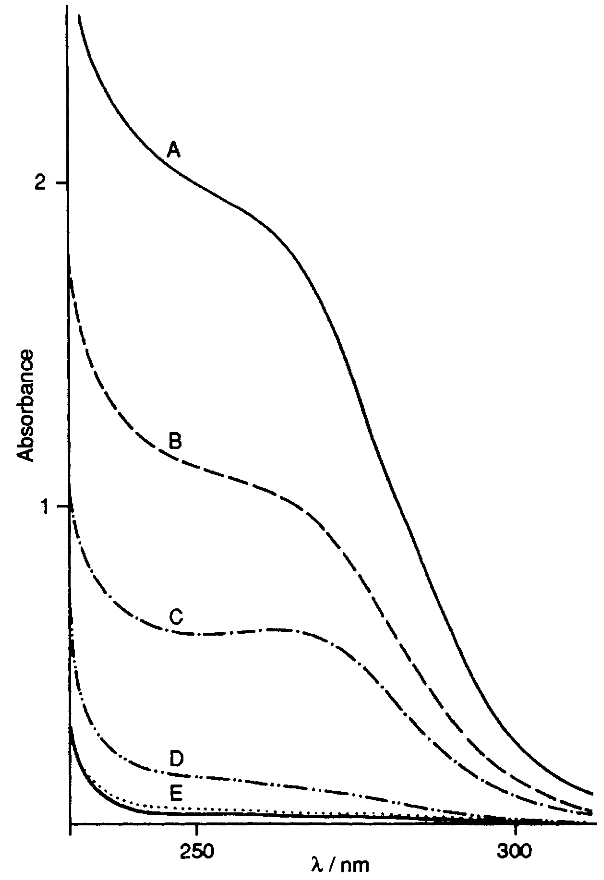

Fig. 1 UV spectra of solutions containing NaOH (6 mol dm^{-3}) (lower full line) and Al^{III} (1 mol dm^{-3}) as detailed in Table 1

A black precipitate was invariably found following aluminium dissolution in NaOH; the lower the purity of the samples the greater the amount of precipitate in most cases. These precipitates were removed by filtration, washed thoroughly with distilled water and dried *in vacuo*. The resultant black powder appeared to be magnetic and EDAX measurements showed that its main components were Al and Fe, although traces of Ti and Si were also detected. Mössbauer spectra indicated that the iron occurred in all of its three common oxidation states, Fe^{III}, Fe^{II} and Fe^0, but the majority was Fe^{III}.†

Representative UV spectra of the supernatant liquids are shown in Fig. 1. These spectra are similar to those published in ref. 9 but differ from those of refs. 7 and 8. A direct correlation between the UV band intensity and aluminium purity is evident. Only when very high purity Al samples are used are the solutions entirely transparent in this spectral range. No spectral changes were observed for aluminium concentrations up to 4 mol dm^{-3} in the case of the 99.999% Al samples. We conclude that all reported UV absorbances for aluminate solutions are due to trace contamination, even with analytical grade materials.

The main UV-active contaminant appears to be dissolved iron. As shown in Fig. 2, spectrum 2, controlled addition of $Fe(ClO_4)_3$ to 6 mol dm^{-3} NaOH solution results in similar, but not identical, spectra to those of the synthetic Bayer liquors. The increase in absorbance with concentration of Fe^{III} obeys the Lambert–Beer law up the point where bulk precipitation occurs. This suggests that the formation of the putative $Fe(OH)_4^-$ complex[10,11] is occurring, prior to precipitation, perhaps as subcolloidal $Fe(OH)_3$,[12] ferrihydrite or goethite.[13] These transformations might well account for the time-dependent spectral behaviour of the Bayer liquors described in ref. 9.

It is, however, clear that the UV spectra of the less pure samples are not due solely to iron species. In particular, there is a significant systematic difference between the apparent concentration of Fe^{III} (calculated from absorbance) and its concentration determined by atomic absorption spectroscopy. This is confirmed by subtracting the contribution of the iron species from the observed spectra of the liquors. A pronounced peak (spectrum 3, Fig. 2) appears with $\lambda_{max} = 270$ nm. This peak is similar to that in the spectra published in refs. 7 and 8. Interestingly, for solutions with low OH^-/Al^{3+} ratios which contain partially precipitated $Al(OH)_3(s)$, a UV peak also appears at *ca.* 270 nm (Fig. 2). We interpret this as being due to the coprecipitation of the iron species with a consequent decrease in absorbance around 230–250 nm. Inductively coupled plasma atomic emission spectroscopy (ICP) measurements confirm that the iron coprecipitates with aluminium. The ICP analysis also showed that some of the common d-block contaminants of aluminium[14] (Cr, Ti, Mn) were not present in our samples and that vanadium was the most likely remaining possibility. This supposition is supported by the UV spectrum of Na_3VO_4 in NaOH (6 mol dm^{-3}), see the inset of Fig. 2, which exhibits almost identical characteristics to spectrum 3, Fig. 2 inset. Given that the absorptivity of VO_4^{3-} is very high ($\varepsilon = 1.3 \times 10^4$ dm^3 mol^{-1} cm^{-1} at $\lambda = 270$ nm), it is clear that even the smallest trace of vanadium in the aluminium metal can produce a significant absorbance.

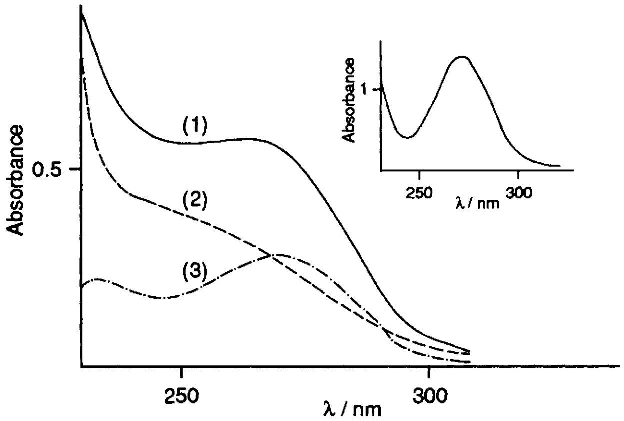

Fig. 2 Decomposition of the UV spectra of synthetic Bayer liquors: (1) NaOH (6 mol dm^{-3}) and Al^{III} (1 mol dm^{-3}) solution containing 80 mmol dm^{-3} dissolved Fe^{III} as determined by atomic absorption spectrometry. (2) NaOH (6 mol dm^{-3}) solution containing 80 mmol dm^{-3} Fe^{III}. (3) The difference between spectrum 1 and spectrum 2. Inset: Spectrum of 0.1 mmol dm^{-3} Na_3VO_4 in NaOH (6 mol dm^{-3}) solution. All spectra recorded with a 10 mm path length against distilled water.

The present observations suggest that in synthetic Bayer liquors, at concentrations typical of aluminate precipitation, all our absorbances can be attributed to trace contaminants. There is no evidence of any contribution to the UV spectra coming from the aluminate species, as has been postulated previously.[7–9] Comments to the contrary in recent work on the determination of the standard molar enthalpy of formation of $Al(OH)_4^-$ (aq)[15] need to be reappraised accordingly.

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Footnote

† A referee has suggested that carbides may be formed but the Mössbauer spectrum suggests this is not likely.

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