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Decomposition of Bayer process organics: Low-molecular-weight carboxylates

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ABSTRACT

The degradation of twenty-one low-molecular-weight organic carboxylates has been studied at 90 and 180 °C, in a synthetic Bayer liquor consisting of 6 mol kg^{-1} aqueous NaOH solution, for periods of up to 36 days. The reactions were monitored and the major degradation products identified by HPLC and NMR spectroscopy. The carboxylates chosen for the study were either possible intermediates or known products arising from the decomposition of organic matter in the Bayer process. Aliphatic carboxylates without hydroxyl substituents were stable at 90 °C but decomposed at 180 °C, except for formate, acetate, oxalate and succinate. The corresponding aromatic carboxylates were stable even at 180 °C. Both aliphatic and aromatic carboxylates with hydroxyl substituents were unstable at 90 °C except for lactate and 4-hydroxy-benzoate. The most frequently detected decomposition products for both aliphatic and aromatic carboxylates were formate, acetate, oxalate, succinate and lactate. Phenolate was also observed for some aromatic carboxylates. These products are briefly discussed with reference to possible mechanisms for the degradation reactions.

1. Introduction

Organic matter enters the Bayer process during dissolution of bauxite ore in concentrated sodium hydroxide solution at elevated temperatures. This is significant as it is well known that the presence of some organic species, particularly oxalate, in Bayer process liquors has deleterious outcomes with respect to both product quality and quantity (Lever, 1978; Guthrie et al., 1984). Even the thermodynamically stable carbonate ion, which is a degradation product of many organic species in hot concentrated caustic solutions, has various negative effects on the Bayer process and must be controlled by costly 're-causticisation' procedures (Hudson, 1987). The impact of organic impurities in Bayer plants is potentially serious even though the amount of organic matter in feedstock ore is generally quite low: ca. 0.05–0.5 wt.% of total organic carbon in Australian bauxites (Whelan et al., 2003a). This is because the caustic liquor is continuously recycled, which creates, under typical process conditions, a dynamic steady-state of the total organic carbon (TOC) load in which inputs and outputs are more or less balanced.

Organic matter in Bayer liquors is derived from two main sources: plant root systems that penetrate deep into the bauxite deposits from overlying vegetation (Ellis et al., 2002a,b) and humic material that has accumulated over the history of the bauxite deposit through geochemical and bacterial transformation of plant and animal matter (Power and Tichbon, 1990; Swift, 1999). The high-molecular-weight organic biopolymers (lignin, cellulose, and humic substances) arising from these sources are quickly degraded during digestion of the bauxite ore to three main types of low-molecular-weight (LMW) organic anions: benzene-carboxylates, phenolates, and aliphatic carboxylates (Lever, 1978; Whelan et al., 2003a). However, these species can react further in the hot concentrated NaOH (aq) to form simpler species. Thus, an understanding of the reactivity of these LMW organics in Bayer liquors is of considerable importance for predicting their effects on the production process and for developing appropriate mitigation procedures, such as selective degradation by wet oxidation.

Most information currently available in the public domain about the LMW organic compounds in Bayer liquors is related to their qualitative identification. Only a few studies have reported on their reactivity or the mechanism(s) by which they are transformed into the more stable species, such as oxalate, acetate and formate, that are routinely found in these liquors (Tardio et al., 2004; Loh et al., 2008a,b). For example, Ellis et al. (2002a,b) identified ca. 50 organic compounds, mainly the anions of organic acids, which could be generated from typical source biopolymers. However, these studies were carried out on a relatively short time scale (48 h, the approximate residence time of liquor in a single Bayer plant cycle) and the identification of so many compounds suggests that some are probably intermediates in the breakdown of biopolymers. As certain amounts of these organic intermediates, along with relatively stable species like acetate and oxalate will remain in the liquor during recycling, it is of interest to explore their longer term behaviour under typical Bayer processing conditions.

Previous studies of the degradation of organic compounds in highly alkaline aqueous solutions used gas chromatography (GC) as the analytical method (Guthrie et al., 1984; Ellis et al., 2002a,b). While

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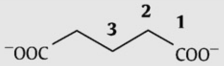
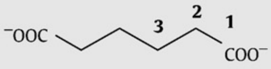
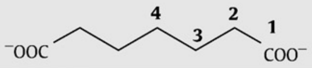
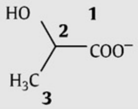
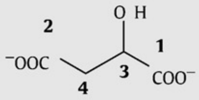
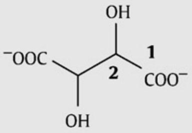
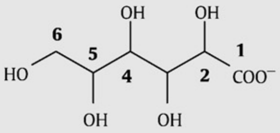
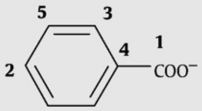
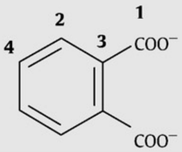
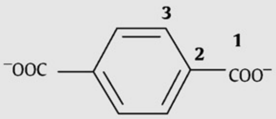
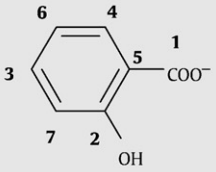
Table 1
^{13}C NMR chemical shifts for the investigated carboxylates in D_2O and 6 m NaOH (aq).[a]

Carboxylate	Structure	Solvent	^{13}C-NMR Chemical Shifts δ_C (carbon number)
Aliphatic			
formate	$H\overset{1}{C}OO^-$	D_2O NaOH	171.0 (1) 171.2 (1)
acetate	$\overset{2}{C}H_3\overset{1}{C}OO^-$	D_2O NaOH	181.3 (1); 23.4 (2) 181.2 (1); 23.8 (2)
malonate	$^-OOC\overset{2}{C}H_2\overset{1}{C}OO^-$	D_2O NaOH	177.4 (1); 47.6 (2) 177.7 (1); 47.8 (2)
succinate	$^-OOC(\overset{2}{C}H_2)_2\overset{1}{C}OO^-$	D_2O NaOH	176.9 (1); 28.6 (2) 182.3 (1); 33.9 (2)
glutarate		D_2O NaOH	177.7 (1); 33.6 (2); 19.5 (3) 182.9 (1); 36.9 (2); 22.6 (3)
adipate		D_2O NaOH	178.6 (1); 33.3 (2); 23.6 (3) 183.6 (1); 37.3 (2); 25.7 (3)
pimelate		D_2O NaOH	178.9 (1); 33.5 (2); 27.5 (3); 23.8 (4) 183.8 (1); 37.4 (2); 28.5 (3); 25.5 (4)
lactate		D_2O NaOH	182.4 (1); 68.3 (2); 20.0 (3) 183.2 (1); 68.2 (2); 20.8 (3)
malate		D_2O NaOH	176.1 (1); 174.1 (2); 66.6 (3); 38.1 (4) 181.1 (1); 179.7 (2); 70.0 (3), 42.4 (4)
tartrate		D_2O NaOH	178.5 (1); 73.6 (2) 180.3 (1); 74.6 (2)
gluconate		D_2O NaOH	178.6 (1); 73.8 (2); 72.2 (3); 70.9 (4); 70.7 (5); 62.3 (6) 180.8 (1); 75.7 (2); 75.1 (3); 72.7 (4); 71.2 (5); 63.5 (6)
Aromatic			
benzoate		D_2O NaOH	175.5 (1); 136.0 (2); 131.1 (3); 128.7 (4); 128.1 (5) 175.3 (1); 135.8 (2); 131.2 (3); 128.7 (4); 128.2 (5)
phthalate		D_2O NaOH	171.9 (1); 131.8 (2); 131.3 (3); 128.7 (4) 177.5 (1); 137.5 (2); 128.8 (3); 127.1 (4)
terephthalate		D_2O NaOH	not soluble 175.4 (1); 138.8 (2); 129.0 (3)
salicylate		D_2O NaOH	175.4 (1); 159.3 (2); 133.6 (3); 130.1 (4); 119.0 (5); 117.7 (6); 115.9 (7) 178.9 (1); 164.8 (2); 130.8 (3); 129.3 (4); 128.4 (5); 120.7 (6); 112.8 (7)