

Solubility of polyaluminium coagulants

David J. Pernitsky and James K. Edzwald

ABSTRACT

This study investigated the solubility characteristics of several polyaluminium coagulants with different chemistries. Solubility in deionized water was studied at 20 and 5°C between pH 4 and 9 for seven coagulants: alum, a low and a high basicity polyaluminium chloride (PACl) containing no sulphate, a medium and a high basicity PACl with sulphate, aluminium chlorohydrate and a low basicity polyaluminium sulphate (PAS). Solubility was defined by measuring the concentration of aluminium passing through a 0.22 µm pore size membrane filter. Aluminium solubility diagrams were produced from the dissolved Al—pH data. Experimental solubility data were compared with published thermodynamic data to infer the Al-species present.

Solubility characteristics differed significantly between the different polyaluminium coagulants. At 20°C, the pH of minimum solubility was 6.0 for alum and PAS, between 6.2 and 6.4 for the PACls, and 6.7 for aluminium chlorohydrate. At 5°C, the pH of minimum solubility increased for all coagulants. Among the PACls, the pH of minimum solubility increased as the basicity increased. The solubility data indicated the presence of the Al_7^{3+} polymer for the high basicity PACls and a mixture of polymers and monomers for the low and medium basicity PACls. There was no evidence of the Al_{13}^{7+} polymer for alum or PAS. The presence of low concentrations of sulphate (2%) in the high basicity PACls did not affect solubility.

Key words | aluminium, aluminium chlorohydrate, coagulation, polyaluminium chloride, polyaluminium sulphate

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INTRODUCTION

Many types of polyaluminium coagulants are commercially available for water and wastewater treatment, including polyaluminium chloride (PACl), aluminium chlorohydrate, polyaluminium sulphate (PAS) and polyaluminium silica sulphate (PASS). Polyaluminium coagulants are produced under carefully controlled conditions by the partial neutralization of aluminium salts. This results in the formation of highly charged polymeric aluminium species that have been shown to be good coagulants for water and wastewater treatment (Bottero *et al.*, 1980b; Dempsey *et al.*, 1984; Bottero & Bersillon, 1989; Van Benschoten & Edzwald, 1990a,b; Edzwald *et al.*, 2000). Unlike alum, polyaluminium coagulants can differ in their basicity and strength, and can contain small amounts of other substances, such as sulphate, silica, and calcium.

During coagulation, reactions that occur during two time scales can be considered. Immediately following coagulant addition, active coagulant species are formed and are dispersed into the bulk flow by rapid mix processes. This occurs on the time scale of seconds (Amirtharajah & Tambo, 1991), and depends on the chemistry of the coagulant species present during the rapid mix process. For example, when alum is added, Al^{3+} hydrolyses in much less than 1 sec (Hahn & Stumm, 1968) to a series of aluminium hydroxides, which become the active coagulant species. For polyaluminium coagulants, the primary coagulant species are preformed, and are immediately available for coagulation reactions.

On a longer time scale, solid-phase particles are formed during flocculation and removed by solid/liquid separation processes such as sedimentation, flotation and

Table 1 | Summary of thermodynamic data for Al hydrolysis reactions

Chemical equation	Equilibrium expression	pK		
		25°C	20°C	5°C
$\text{Al}(\text{OH})_{3(\text{am})} \leftrightarrow \text{Al}^{3+} + 3\text{OH}^{-}$	$K_{\text{so}} = [\text{Al}^{3+}][\text{OH}^{-}]^3$	31.50 ^a	31.67	32.40
$\text{Al}^{3+} + \text{H}_2\text{O} \leftrightarrow \text{AlOH}^{2+} + \text{H}^{+}$	$K_{11} = [\text{AlOH}^{2+}][\text{H}^{+}]/[\text{Al}^{3+}]$	5.00 ^b	5.12	5.65
$\text{Al}^{3+} + 2\text{H}_2\text{O} \leftrightarrow \text{Al}(\text{OH})_2^{+} + 2\text{H}^{+}$	$K_{12} = [\text{Al}(\text{OH})_2^{+}][\text{H}^{+}]^2/[\text{Al}^{3+}]$	10.10 ^b	10.45	11.56
$\text{Al}^{3+} + 4\text{H}_2\text{O} \leftrightarrow \text{Al}(\text{OH})_4^{-} + 4\text{H}^{+}$	$K_{14} = [\text{Al}(\text{OH})_4^{-}][\text{H}^{+}]^4/[\text{Al}^{3+}]$	22.99 ^b	23.58	25.33
$13\text{Al}^{3+} + 28\text{H}_2\text{O} \leftrightarrow \text{Al}_{13}(\text{OH})_{24}^{7+} + 32\text{H}^{+}$	$K = [\text{Al}_{13}^{7+}][\text{H}^{+}]^{32}/[\text{Al}^{3+}]^{13}$	98.73 ^c	102.2	113.4

^aSource: Van Benschoten & Edzwald (1990a).^bSource: Nordstrom & May (1996).^cSource: Baes & Mesmer (1976).

filtration. Over typical water treatment plant detention times of tens to hundreds of minutes, coagulant species approach an equilibrium state between the dissolved and solid phases. This equilibrium chemistry is especially important for control of dissolved aluminium residuals after treatment.

The purpose of the research was to investigate the solubility characteristics of several commercially available polyaluminium coagulants. This paper focuses on the equilibrium chemistry of alum and polyaluminium coagulants in deionized water. Interactions with NOM, particles and other dissolved species such as F^{-} , PO_4^{3-} , etc., were not considered. Although natural waters contain many dissolved chemical species that can affect solubility, deionized water was used for this research to provide baseline solubility data, and highlight differences in solubility between the different coagulants examined.

Alum chemistry

The chemistry of aluminium coagulants in water is governed by the hydrolysis characteristics of aqueous Al(III). In dilute solutions, free aluminium forms a series of monomeric aluminium hydroxide species in equilibrium with an amorphous aluminium hydroxide precipi-

tate. Several studies have concluded that alum solubility can be adequately described by the presence of three monomeric Al species: Al^{3+} , $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_4^{-}$ in equilibrium with an amorphous $\text{Al}(\text{OH})_{3(\text{am})}$ solid phase (Hayden & Rubin, 1974; Van Benschoten & Edzwald, 1990a). Formation reactions and thermodynamic constants for these species are summarized in Table 1. These reactions are thought to be rapid and reversible in dilute solutions (<0.001 M) (Baes & Mesmer, 1976).

Chemistry of polyaluminium coagulants

Polyaluminium coagulants are characterized by their degree of neutralization (r), or basicity:

$$r = [\text{OH}^{-}]/[\text{Al}_T], \quad (1)$$

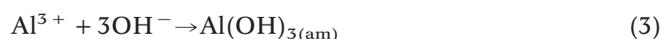
where $[\text{OH}^{-}]$ represents base added during production

$$\text{basicity} = (r/3) \times 100\% \quad (2)$$

The value for r can vary from 0 to 3, corresponding to basicities of 0 to 100%. Commercial polyaluminium coagulants are generally available with basicities between 15 and 85%. The basicity affects the alkalinity consumption of the coagulant, as well as the relative prevalence of

polymeric and monomeric species. In general, the higher the basicity the greater the fraction of polymeric species, up to an r of approximately 2.1 (70% basicity) (Bottero *et al.*, 1980a).

At an r value of 3, precipitation of amorphous $\text{Al}(\text{OH})_{3(\text{am})}$ is predicted according to the following stoichiometry:



A tridecameric Al_{13} species with the formula $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ (abbreviated as Al_{13}^{7+}) has been shown to be the dominant polymeric species in partially neutralized Al solutions (Parthasarathy & Buffle, 1985; Bertsch *et al.*, 1986; Bertsch, 1987; Van Benschoten & Edzwald, 1990a; Parker & Bertsch, 1992a,b). The Al_{13}^{7+} polymer is composed of a tetrahedrally coordinated Al atom located at the centre of a cage of 12 octahedrally coordinated Al atoms (Johansson, 1960). Thermodynamic data for the formation of the Al_{13}^{7+} polymer are shown in Table 1. Other polymers have been proposed and may exist in some solutions at certain r values (Hsu & Bates, 1964; Smith, 1971; Hyaden & Rubin, 1974; Baes & Mesmer, 1976; Bottero *et al.*, 1980a; Allouche *et al.*, 2000), but they represent only a small fraction of the total polymeric aluminium (Bottero *et al.*, 1980a).

Early studies on the production of PACl found that the yield of Al_{13}^{7+} and its stability after production are sensitive to the synthesis conditions (Parthasarathy & Buffle, 1985; Bertsch, 1987; Parker & Bertsch, 1992a; Clark *et al.*, 1993). It is thought that the initial synthesis of the tridecamer depends on an optimal concentration of precursors, probably including tetrahedrally co-ordinated $\text{Al}(\text{OH})_4^{1-}$ species (Parker & Bertsch, 1992a). Bertsch (1987) concluded that the production of Al_{13}^{7+} requires non-homogeneous conditions at the point of base introduction that allow Al to exist in tetrahedral co-ordination. The formation of Al_{13}^{7+} and its conversion to a solid phase has been summarized by Bertsch & Parker (1996). Unlike Al-monomers, polymeric species are often metastable, and do not reach equilibrium with a thermodynamically stable solid phase rapidly (Smith, 1971; Bertsch, 1987; Van Benschoten & Edzwald, 1990a; Parker & Bertsch, 1992b).

Solid phases

After the initial coagulation reactions are complete, all of the monomeric and polymeric species described above approach equilibrium with one or more solid phases of $\text{Al}(\text{OH})_3$, in oversaturated solutions. The addition of aluminium coagulants to water in excess of the solubility limit results in the formation of an amorphous aluminium trihydroxide, $\text{Al}(\text{OH})_{3(\text{am})}$. There is some evidence that the solid phases formed by the precipitation of alum and PACl are different, and that some of the characteristics of the Al_{13}^{7+} polymer are retained when PACl precipitates (Bottero *et al.*, 1980a; Van Benschoten & Edzwald, 1990a). The presence of other anions such as SO_4^{2-} , PO_4^{3-} and organics in solution has been shown to alter the precipitation behaviour of both monomeric and polymeric species (Letterman & Vanderbrook, 1983; Duffy & van Loon, 1994; Bertsch & Parker, 1996). An amorphous precipitate with a $\log K_{\text{so}}$ of -31.5 (25°C) has been found to agree with aluminium solubility data obtained under drinking water treatment conditions (Van Benschoten & Edzwald, 1990a).

Effects of sulphate

Sulphate is present in several aluminium coagulants. Dry alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 14 \text{H}_2\text{O}$) has a sulphate content of approximately 48% (liquid alum typically contains approximately 23–24%). Sulphate can also be added to PACl coagulants in small amounts (typically <5%). Sulphate concentrations in PAS are slightly less than in alum.

Sulphate is a tetrahedral polyvalent anion, the presence of which affects the hydrolysis-precipitation reactions of Al(III) solutions (Hayden & Rubin, 1974; Letterman & Vanderbrook, 1983; Hundt & O'Melia, 1988). In the presence of the sulphate anion, less base is necessary to produce a visible precipitate than when monomeric Al(III) solutions containing chloride or nitrate are titrated with base. The pH range over which the precipitate is present also broadens with sulphate addition. These effects have been attributed to the formation of insoluble sulphatohydroxo-aluminium(III) species of the form $\text{Al}_x(\text{SO}_4)_y(\text{OH})_z^{(3x-2y-z)+}$, where the sulphate ion enters

into the co-ordination sphere of the aluminium ion in place of hydroxyl ions (Hayden & Rubin, 1974). Mechanistically, it has also been proposed that sulphate acts as a catalyst, lowering the activation energy for the conversion of Al^{3+} to $\text{Al}(\text{OH})_{3(s)}$ (De Hek *et al.*, 1978). Sulphate also forms outer-sphere adsorption complexes on aluminium oxides, and the sorbed sulphate can destabilize colloidal suspensions (De Hek *et al.*, 1978).

The presence of sulphate also affects the chemistry of polymeric aluminium solutions. When sulphate is added to solution before polymer synthesis, Al_{13}^{7+} formation has been reported to decrease, whereas sulphate added after synthesis had no effect on Al_{13}^{7+} formation (Kerven *et al.*, 1995). Others have found that high concentrations of sulphate react with Al_{13}^{7+} to form an insoluble Al_{13} -sulphate salt (Furrer *et al.*, 1992). The addition of sulphate prior to titration of a PACl coagulant has been reported to shift Al speciation from mostly medium-size polymers for the no-sulphate case, to mostly $\text{Al}(\text{OH})_{3(s)}$ for the sulphated case, in the pH range of 4.75 to 7.0 (Hundt & O'Melia, 1988). In water treatment practice, the use of PACls containing small amounts of sulphate resulted in the formation of rapidly settling floc and improved treatment by sedimentation compared with non-sulphated PACls (Edzwald *et al.*, 2000). Some of these observations may be explained by the fact that the sulphate anion neutralizes the positive charge of Al_{13}^{7+} cations at the surface of particles, reducing the fractal dimensions of the resulting aggregate (Waite *et al.*, 2001).

PAS can be produced by the titration of aluminium sulphate (alum) by strong base. Studies on PAS speciation have concluded that most PAS coagulants contain Al monomers and small polymers, but that Al_{13}^{7+} does not form in most PAS preparations (Dempsey, 1994).

METHODS

Coagulants used

The coagulants used in this research represented a cross-section of the commercial polyaluminium coagulants commonly used for drinking water treatment: alum, a low and a high basicity polyaluminium chloride containing no

sulphate (LBNS and HBNS PACls), a medium and a high basicity PACl with approximately 2% wt sulphate (MBS and HBS PACls), aluminium chlorohydrate and a low basicity polyaluminium sulphate (PAS). All coagulants used in this research were prepared and supplied by Holland Company Inc. (North Adams, MA), Kemwater North America (Savannah, GA) and Kemira Kemi AB (Helsingborg, Sweden). Coagulant specifications and the abbreviations used to refer to them in the text are summarized in Table 2.

Aluminium solubility experiments

Solubility over a pH range of 4 to 9 at both 5 and 20°C was determined for all coagulants. Solubility was determined by adding a known amount of aluminium coagulant to high quality reagent water (Super-Q, Millipore Corporation, Bedford, MA, USA) and measuring the dissolved aluminium concentration after a slow mixing period of 90 min to represent detention times for flocculation and settling in water treatment plants. A coagulant dose of 5×10^{-4} M Al was added to 200 ml of high quality reagent water in 250 ml glass beakers, under intense mixing conditions with a magnetic stir bar. This coagulant dose corresponds to approximately 150 mg/l for alum. Immediately after coagulant addition, pH was adjusted to between 4 and 9 with HCl (1.0 N), NaHCO_3 (0.2 N), or NaOH (1.0 N). The order of addition of the coagulant and the pH adjustment chemicals was reversed for selected experiments and found not to affect the solubility results (Pernitsky, 2001). Chemical addition was followed by 2 min of rapid mixing. After mixing, beakers were transferred to a Phipps and Bird PB900 programmable jar test apparatus (General Medical Manufacturing Company, Richmond, VA, USA) for 90 min of slow mixing at 50 rpm. At the end of the slow mixing period, samples were taken (without settling), filtered through a 0.22 μm membrane filter (Supor-200, Gelman Sciences, Ann Arbor, MI, USA), and the dissolved aluminium remaining in solution was measured.

Total and dissolved aluminium were measured colorimetrically by 8-hydroxyquinoline and butyl acetate extraction (Van Benschoten & Edzwald, 1990c), using a

Table 2 | Coagulant specifications

Coagulant	Symbol	Strength (% wt as Al ₂ O ₃)	Specific gravity	Basicity (%)	Sulphate (% wt)
Liquid alum	Alum	8.3	1.33	0	23.5
PACl low basicity non-sulphated	LBNS	10.0	1.24	12–30	0
PACl medium basicity sulphated	MBS	10.0	1.20	38–45	2.5
PACl high basicity non-sulphated	HBNS	10.0	1.24	62–75	0
PACl high basicity sulphated	HBS	10.0	1.24	60–70	1.8
Aluminium chlorohydrate	—	24.0	1.36	83	0
PAS low basicity	PAS	7.6	1.37	30	21–22

Perkin Elmer Lambda 3 Spectrophotometer (Perkin Elmer, Norwalk, CT, USA). It should be noted that the use of a 0.22 µm filter to distinguish particulate and dissolved forms of Al is clearly an operational definition. A 0.45 µm pore size has traditionally been used to define soluble materials. However, it has been shown that concentrations of dissolved metals usually decrease with smaller pore-size filters (Kennedy & Zellweger, 1974; James *et al.*, 1985). A smaller pore-size filter was used in this research to minimize misclassification. This is consistent with other studies of drinking water coagulation (Dempsey *et al.*, 1984; Van Benschoten & Edzwald, 1990a,c). The presence of microcrystalline particles of Al(OH)_{3(s)} ranging in size from 10 to 2000 Å has been reported after PACl addition (Parthasarathy & Buffle, 1985). Although colloidal particles of this size are not typically considered floc particles, they could pass through the 0.22 µm filter, if present, and be incorrectly classified as dissolved Al.

The 5°C experiments were conducted in a cold temperature room (Norlake, Hudson, WI, USA) to maintain uniform temperature conditions. pH was measured using an Orion Model 520A pH Meter (Orion Research Incorporated, Boston, MA, USA), equipped with an Orion Model 91-57BN Triode pH low ionic strength electrode.

The dissolved aluminium data are summarized in the form of solubility diagrams. Plotted along with the exper-

imental results is the theoretical distribution of aluminium species based on thermodynamic data obtained from the literature. The thermodynamic data used are summarized in Table 1 for reference. Temperature adjustment of the thermodynamic data was performed using the Van't Hoff equation, where heats of formation were available in the cited reference. If heats of formation were not available in the original reference, the empirical temperature functions presented in Nordstrom & May (1996) were used. Ionic strength effects were negligible under the experimental conditions ($I < 5 \times 10^{-4}$), and therefore no adjustments to the thermodynamic data were made.

From the experimental data, the pH of minimum solubility and the minimum solubility for each coagulant were determined as follows. As shown in Figure 1, lines A and B were determined for each experiment by performing linear regression (Microsoft Excel 7.0) on the experimental data points. The calculated point of intersection between lines A and B was used to define the point of minimum solubility.

RESULTS AND DISCUSSION

Figures 2 through 9 present the experimental results in the form of solubility diagrams. In order to help the reader

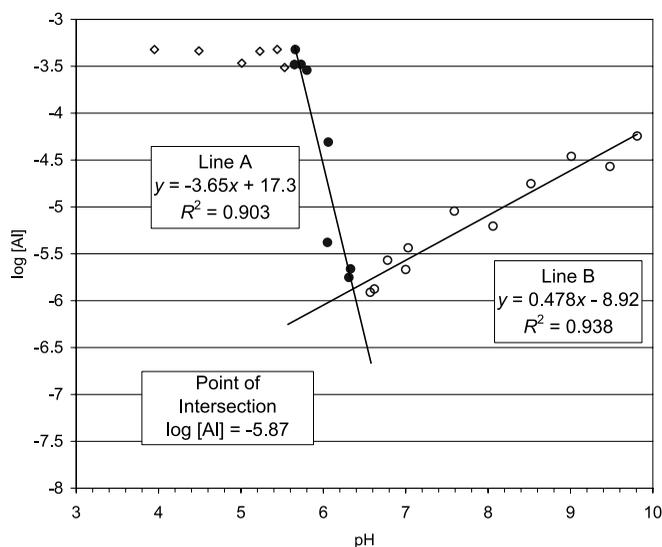


Figure 1 | Example regression calculations for solubility experiments (HBNS at 20°C shown).

understand the relationships between the experimental solubility results and the possible Al-species present, theoretical lines for three dissolved species, $\text{Al}(\text{OH})_2^{2+}$, Al_{13}^{7+} and $\text{Al}(\text{OH})_4^{1-}$ in equilibrium with $\text{Al}(\text{OH})_{3(\text{am})}$, are also shown. These species, along with Al^{3+} , have the largest effect on total solubility over the pH range investi-

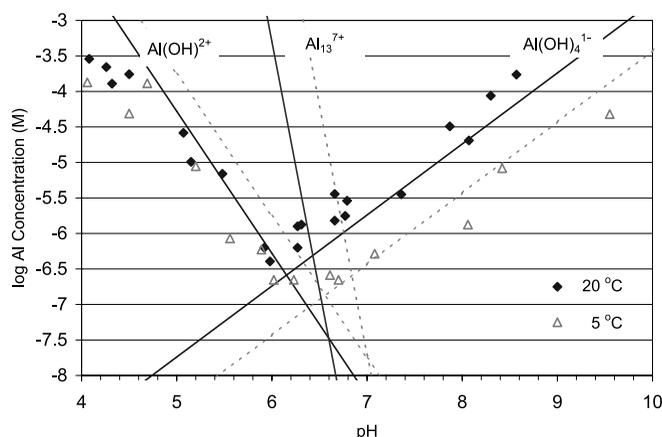


Figure 2 | Experimental solubility data at 20 and 5°C for dissolved aluminium in solutions of alum (alum added at $\log [\text{Al}] = -3.30$). Theoretical solubility for Al species in equilibrium with $\text{Al}(\text{OH})_{3(\text{am})}$ indicated by solid (20°C) and dashed (5°C) lines. pK_{50} values are summarized in Table 1.

gated in this research. To maintain readability, the lines for Al^{3+} are not shown. The calculated values of the pH of minimum solubility and the minimum solubility for each coagulant are summarized in Table 3.

As shown in Figures 2 and 3, alum and PAS showed similar solubility. Above the pH of minimum solubility, the data agreed with the solubility predicted by $\text{Al}(\text{OH})_4^{1-}$ in equilibrium with $\text{Al}(\text{OH})_{3(\text{am})}$ at both temperatures

Table 3 | Summary of measured coagulant solubility

Coagulant	Minimum solubility 20°C		Minimum solubility 5°C	
	pH	µg/l Al	pH	µg/l Al
Alum	6.0	16	6.2	3
PAS	6.0	28	6.4	6
LBNS	6.2	27	6.7	4
MBS	6.3	29	6.5	4
HBNS	6.4	36	6.8	9
HBS	6.4	52	6.9	5
Al-chlorohydrate	6.7	101	7.6	53

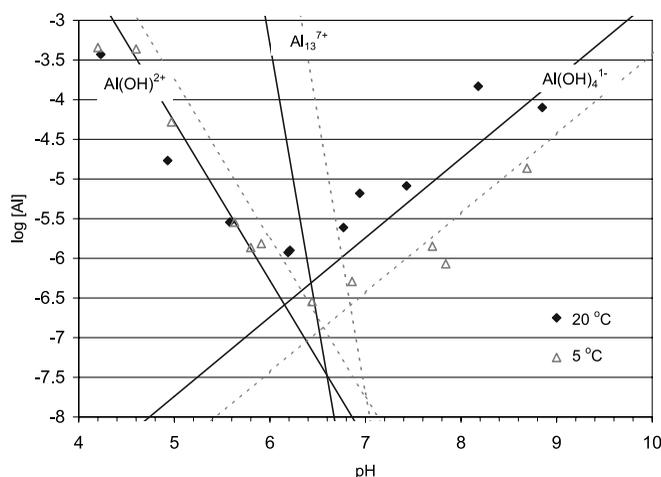


Figure 3 | Experimental solubility data at 20 and 5°C for dissolved aluminium in solutions of low basicity PAS (PAS added at $\log [\text{Al}] = -3.30$). Theoretical solubility for Al species in equilibrium with $\text{Al}(\text{OH})_{3(\text{am})}$ indicated by solid (20°C) and dashed (5°C) lines. pK_{50} values are summarized in Table 1.

tested. For both of these coagulants, better agreement between the data and the theoretical solubility line for $\text{Al}(\text{OH})^{2+}$ was seen at 20°C than at 5°C. For pH less than the pH of minimum solubility, the increase in solubility predicted at the lower temperature by the thermodynamic data for $\text{Al}(\text{OH})^{2+}$ was not observed. This result is not in agreement with previously published solubility data (Van Benschoten & Edzwald, 1990a). Overall, as shown in Table 3, the pH of minimum solubility and the minimum solubility both increased at 5°C compared to 20°C. A smaller shift was seen in this research than reported by others (Van Benschoten & Edzwald, 1990a). Alum and PAS solubility can be described by the chemical species Al^{3+} , $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_4^{1-}$. As expected, the data do not indicate the presence of Al_{13}^{7+} for these coagulants.

Figures 4 and 5 show the solubility results for the high basicity PACs (HBNS and HBS). These results are significantly different than those for alum shown in Figure 2. It was expected that the high basicity PACs would have the highest proportion of polymers, since it has been shown that during PACl production, the polymeric fraction increases with increasing basicity (Bottero *et al.*, 1980a). The high basicity PACs do not begin to form a filterable precipitate until pH 5.8 to 6, and as shown in Table 3, have

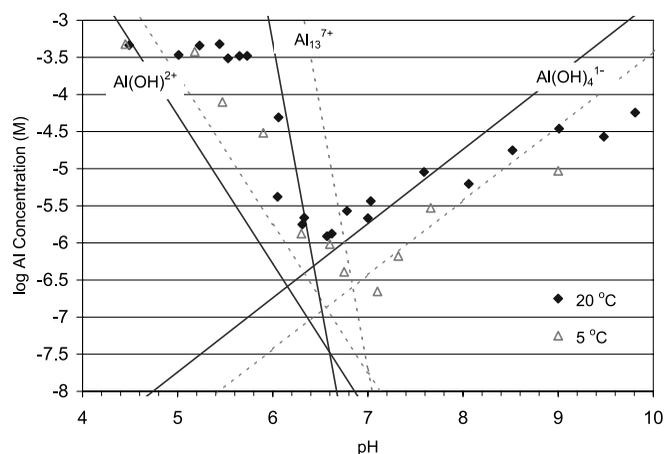


Figure 4 | Experimental solubility data at 20 and 5°C for dissolved aluminium in solutions of HBNS PACl (HBNS added at $\log [\text{Al}] = -3.30$). Theoretical solubility for Al species in equilibrium with $\text{Al}(\text{OH})_{3(\text{am})}$ indicated by solid (20°C) and dashed (5°C) lines. pK_{50} values are summarized in Table 1.

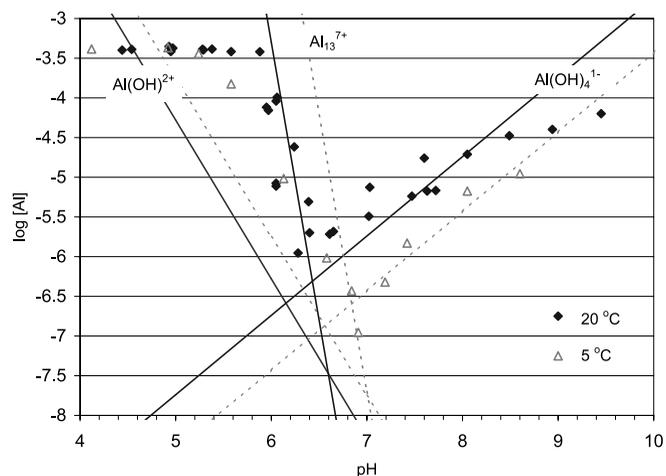


Figure 5 | Experimental solubility data at 20 and 5°C for dissolved aluminium in solutions of HBS PACl (HBS added at $\log [\text{Al}] = -3.30$). Theoretical solubility for Al species in equilibrium with $\text{Al}(\text{OH})_{3(\text{am})}$ indicated by solid (20°C) and dashed (5°C) lines. pK_{50} values are summarized in Table 1.

a higher pH of minimum solubility than alum. In general, the HBNS and HBS data show good agreement with the theoretical line for Al_{13}^{7+} , especially for 20°C. The measured soluble Al did not exhibit a shift to higher pH at 5°C as predicted by the Al_{13}^{7+} thermodynamic data. Reasonable agreement with the $\text{Al}(\text{OH})_4^{1-}$ thermodynamic data was seen for the high basicity PACs, although some deviations from theory were seen at pH greater than 8.

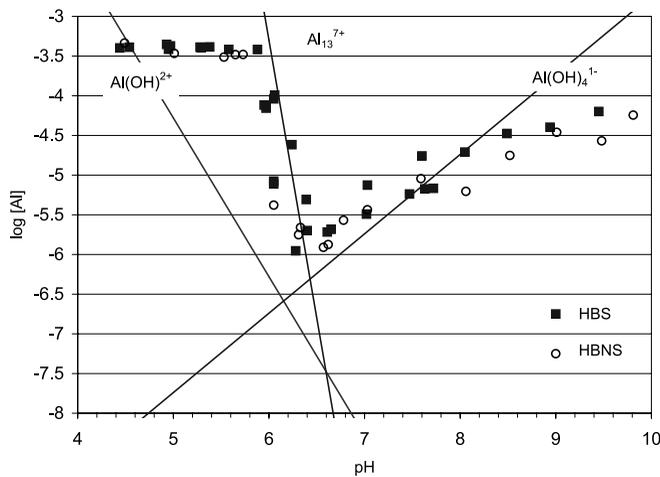


Figure 6 | Comparison of experimental solubility data at 20°C for dissolved aluminium in solutions of HBNS and HBS PACl (PACls added at $\log [Al] = -3.30$). Theoretical solubility for Al species in equilibrium with $Al(OH)_3(am)$ at 20°C indicated by solid lines. pK_{50} values are summarized in Table 1.

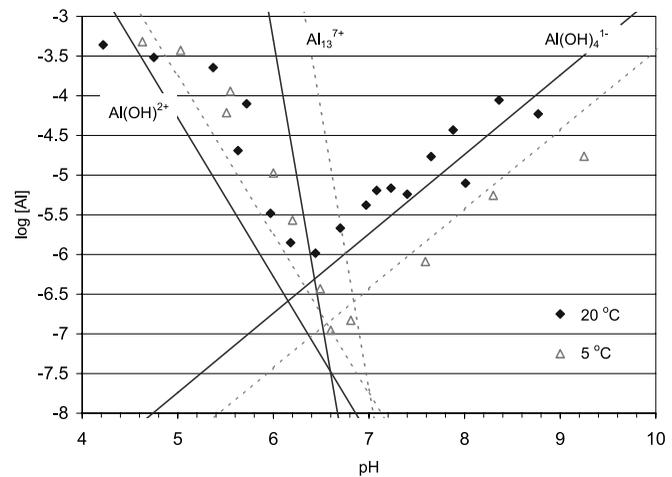


Figure 7 | Experimental solubility data at 20 and 5°C for dissolved aluminium in solutions of LBNS PACl (LBNS added at $\log [Al] = -3.30$). Theoretical solubility for Al species in equilibrium with $Al(OH)_3(am)$ indicated by solid (20°C) and dashed (5°C) lines. pK_{50} values are summarized in Table 1.

This may be due to the formation of a solid phase slightly different than $Al(OH)_3(am)$. Others have reported that the solid phase produced by precipitation of PACls is polymeric in nature, and has different thermodynamic properties (Van Benschoten & Edzwald, 1990a). A comparison of the solubility data for HBNS and HBS shown in Figure 6 and Table 3 indicates that the presence of small amounts of sulphate did not affect the solubility characteristics of the high basicity PACls after 90 min.

Figures 7 and 8 show the solubility data for the low and medium basicity PACls (LBNS and MBS). The results for these coagulants were not well described by either $Al(OH)_2^+$ or Al_{13}^{7+} for pH 5–7. The measured soluble Al tended to fall between the theoretical lines for $Al(OH)_2^+$ and Al_{13}^{7+} . This suggests that a combination of monomers and Al_{13}^{7+} , or some other Al-species, was present. This is expected, since these coagulants contain both monomeric and polymeric aluminium, and the monomeric species would be expected to form a filterable precipitate near pH 5. Again, little difference was seen between the 5 and 20°C results for pH less than 6.5. Above the pH of minimum solubility, the solubility of the LBNS was similar to that of alum.

The aluminium chlorohydrate data, shown in Figure 9, do not show good agreement with the theoretical Al_{13}^{7+}

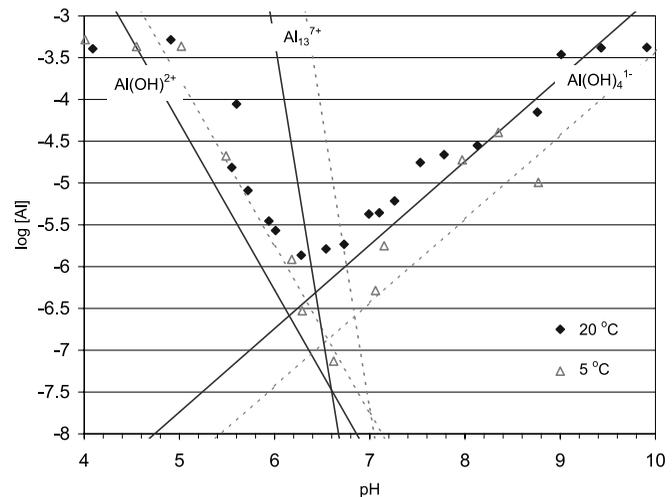


Figure 8 | Experimental solubility data at 20 and 5°C for dissolved aluminium in solutions of MBS PACl (MBS added at $\log [Al] = -3.30$). Theoretical solubility for Al species in equilibrium with $Al(OH)_3(am)$ indicated by solid (20°C) and dashed (5°C) lines. pK_{50} values are summarized in Table 1.

line. For pH less than the pH of minimum solubility, the slope of the data points is less than the slope of 7 expected for the Al_{13}^{7+} polymer, and the measured soluble Al was higher than predicted by theory. As mentioned above, these deviations may be due to the presence of Al-species other than those examined here. For aluminium chlorohydrate, it is possible that a solid species other than

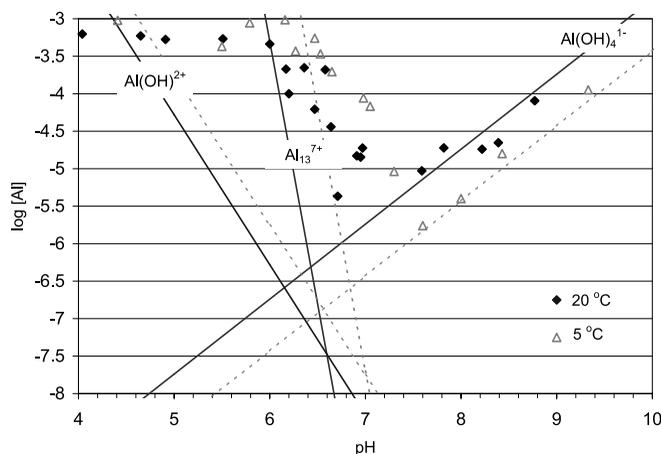


Figure 9 | Experimental solubility data at 20 and 5°C for dissolved aluminium in solutions of aluminium chlorohydrate (Al-chlorohydrate added at $\log [Al] = -3.30$). Theoretical solubility for Al species in equilibrium with $Al(OH)_3(am)$ indicated by solid (20°C) and dashed (5°C) lines. pK_{50} values are summarized in Table 1.

$Al(OH)_3(am)$, and having a pK different than 31.5, may have formed upon precipitation. This is consistent with the results of others who have reported that a non-settling gel is formed at $r > 2.3$ (Bottero *et al.*, 1980a). It is also possible that very small Al-species passed through the 0.22 μm filter and were able to react with 8-hydroxyquinoline. These microcrystalline particles would be expected to have higher solubility due to the higher surface free energy of the solid. Above pH 8, the measured soluble Al showed good agreement with the theoretical solubility line for $Al(OH)_4^-$.

For all of the coagulants except aluminium chlorohydrate, there was no observable effect of temperature on solubility at pH less than the pH of minimum solubility. A satisfactory explanation is not available for this observation. As discussed above, this is not in agreement with previously published Al solubility data. It may be possible that at low temperature and acidic conditions, the 90 min slow mixing time was not adequate for chemical equilibrium to be achieved. No data are available to confirm this. It is also possible that a systematic error between the 5 and 20°C experiments was responsible for this observation, although temperature effects were seen for the aluminium chlorohydrate.

SIGNIFICANCE OF RESULTS

The solubility results reported here can be used in water treatment practice to aid in determining the appropriate coagulation conditions. The significance of these results is discussed below in terms of coagulation mechanisms, the control of dissolved aluminium residuals and the alkalinity consumption associated with coagulant addition.

Coagulation mechanisms

Effective coagulation with alum or polyaluminium coagulants depends on the interaction of the aluminium coagulant species with particles and dissolved organic material in the raw water. This is thought to occur via four primary mechanisms: enmeshment of colloids into floc particles, charge neutralization of colloids by positively charged coagulant species, adsorption of NOM on to the surface of floc particles, and the complexation/precipitation of NOM with positively charged coagulant species (Edzwald, 1992). Solubility data can provide guidance in explaining the coagulation mechanisms that may be present under different chemical conditions, by predicting the pH conditions where large amounts of floc are expected versus conditions where dissolved species predominate. For example, as PACls do not precipitate significantly at pH less than 6 to 6.5, enmeshment of colloids and adsorption of NOM will only be significant coagulation mechanisms at higher pH.

Dissolved residual Al

The results of this research are useful for determining the proper pH conditions for minimizing dissolved residual Al in treated water. With the exception of the aluminium chlorohydrate, the minimum solubilities of the coagulants examined here are very low ($< 50 \mu g/l$ Al at 20°C). PACls are slightly more soluble than alum and PAS at 20°C, while at 5°C there is little difference among coagulants. If coagulation is practised near the coagulant's pH of minimum solubility, current North American and European residual Al targets should be met (US EPA, 1991; European Council, 1998). The appropriate pH for minimizing

residual Al will be lower for alum and PAS than for PACls. Among the PACls, slightly lower pH is appropriate for low and medium basicity PACls than for high basicity PACls. In addition, since the pH of minimum solubility increases at lower temperatures, water treatment plant operators should adjust coagulation pH to account for water temperature. It should also be noted that low pH coagulation (approximately pH 5.5), recommended for enhanced TOC removal with aluminium coagulants, can result in high dissolved residual Al concentrations with all aluminium coagulants, but especially with high basicity PACls and aluminium chlorohydrate.

pH depression

The addition of 1 mg/l of alum results in the consumption of 0.5 mg/l of alkalinity (as CaCO_3). If the raw water alkalinity is low, the alum dose required to achieve proper treatment may depress the pH to below the pH of minimum solubility, requiring subsequent base addition for proper coagulation performance and residual Al control. pH depression is less of a problem with PACls, as they are already partially neutralized, and therefore consume less alkalinity. Among PACls, alkalinity consumption is inversely proportional to basicity. For example, a PACl with 50% basicity will consume only 0.25 mg/l of alkalinity (as CaCO_3). This makes high basicity PACls well suited to low alkalinity waters. Little or no pH adjustment may be necessary to reach the pH of minimum solubility if a high basicity PACl is used for a low or moderate-alkalinity water. Using the alkalinity consumption associated with a given coagulant and the raw water alkalinity, the resulting coagulation pH using various coagulant doses can be predicted using computational models (Najm, 2001).

CONCLUSIONS

This study investigated the solubility characteristics and Al-speciation of several types of polyaluminium coagulants of different basicity and sulphate content. The major conclusions of the solubility experiments were as follows:

- The PACls had a higher pH of minimum solubility than alum or PAS.
- For the PACls, the pH of minimum solubility increased as basicity increased.
- The presence of small amounts of sulphate in PACl did not affect coagulant solubility.
- The pH of minimum solubility increased for all coagulants as temperature decreased.

Based on a comparison of measured soluble Al to published thermodynamic data, the following conclusions can be made:

- The high basicity PACls showed the best agreement with published thermodynamic data for Al_{13}^{7+} .
- The low and medium basicity PACls showed a mixture of monomers and polymers.
- No evidence of the Al_{13}^{7+} polymer was seen for alum or PAS.

The results of this research can be used in practice to determine the appropriate coagulation pH for control of Al-residuals.

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