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NOTES

EFFECT OF TEMPERATURE ON THE DEGRADATION OF Al_{13} COMPLEX

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INTRODUCTION

Partially hydrolyzed Al salt solutions have many applications in pharmaceutical, petroleum, water treatment and other industries. The polynuclear OH-Al complexes present in solution have been recognized as the effective components in industrial applications, but their nature has not been fully understood. Different OH-Al complexes might be present in different OH-Al solutions, and different industrial applications might require different complexes to achieve optimal effectiveness.

Two structural models for the polynuclear OH-Al complexes have been proposed by Hsu (1989). One is the Al_{13} complex of Keggin structure, having a composition $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$. The other is the $Al(OH)_3$-fragment structure, with its Al^{3+} ions distributed in hexagonal rings, sandwiched between 2 OH^- planes. Based upon the kinetics of Al-hydroxyquinoline (Turner 1976) or Al-ferron (Tsai and Hsu 1985) color development, it has been reported that the soluble complexes in freshly prepared OH-Al solutions slowly converted to more stable but still reactive species during prolonged aging. Denney and Hsu (1986) and Wang and Hsu (1994) showed that only the initial unstable complexes in freshly prepared OH-Al solutions yielded a peak in their nuclear magnetic resonance (NMR) spectra with its chemical shift corresponding to tetrahedrally coordinated Al; the stable complexes in aged solutions did not. They suggested that the initial complexes were of Al_{13} structure, while the more stable components formed later were of Al $(OH)_3$-fragment structures. The unstable Al_{13} complex was developed due to localized high alkalinity (Akitt and Farthing 1981; Teagarden et al. 1981; Bertsch 1987; Parker and Bertsch 1992. The transformation of this unstable Al_{13} complex to the more stable $Al(OH)_3$-fragment structure was very slow at room temperature. Probably for this reason, most of the studies of polynuclear OH-Al complexes have focused on the unstable Al_{13} complexes in OH-Al solutions freshly hydrolyzed in the laboratory. The objective of this study is to show that the rate of the transformation from rapid- to slow-reacting complexes was greatly accelerated by an increase in temperature.

EXPERIMENTAL

A laboratory hydrolyzed solution of OH/Al molar ratio = 2 and 0.02 *M* in Al was prepared by the dropwise addition of 800 mL of 0.1 *M* NaOH to 400 mL of a 0.1 *M* $AlCl_3$ solution at a rate of 1 mL/min, followed by dilution to 2000 mL. This solution was split into 5 portions 5 d after preparation. One portion was aged at room temperature as a control. The other 4 portions were heated at 45, 60, 75 and 90 °C, respectively, and analyzed periodically for Al speciation, pH and turbidity up to 166 h. After heating, all solutions were allowed to age further at room temperature and analyzed after 195 and 442 d. Al speciation was based on the kinetics of Al-ferron color development. In this procedure, 0.5 mL of sample aliquot was pipetted into a polyethylene bottle containing 80 mL of ferron reagent and 119.5 mL of H_2O. The absorbance at 366 nm was monitored with time for at least 3 d, until all soluble complexes fully reacted. Such lengthy monitoring of the absorbance is essential for distinguishing solids from slow-reacting soluble complexes. The detailed procedure was published in Wang and Hsu (1994).

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Table 1. Changes in Al species distribution (%) with time as a function of aging temperature.

Aging		Mono‡	Rapid‡		Slow‡	
Temp.,°C	Duration	%	%	k, h^{-1}	%	k, h^{-1}
Initial		18.9	79.0	4.63	2.1	0.0616
45	22 h	18.5	77.6	4.02	3.9	0.0644
45	46 h	19.5	75.9	4.03	4.6	0.0497
45	70 h	20.4	74.5	3.50	5.1	0.0509
45	166 h	23.1	68.2	2.60	8.8	0.0478
RT†	195 d	22.5	55.0	4.10	22.5	0.0488
RT	442 d	21.8	43.0	3.80	35.2	0.0298
60	22 h	21.2	72.6	3.91	6.2	0.0390
60	46 h	20.9	69.2	3.25	9.9	0.0300
60	70 h	19.5	65.5	3.94	15.0	0.0390
60	94 h	22.2	59.7	4.71	18.1	0.0450
RT†	195 d	22.4	51.2	4.35	26.4	0.0415
RT	442 d	22.1	37.2	4.55	40.6	0.0386
75	22 h	19.4	61.4	4.02	19.2	0.0372
75	46 h	20.2	46.7	3.97	33.1	0.0392
75	70 h	23.9	34.8	3.14	41.3	0.0320
75	166 h	21.9	13.7	3.44	64.4	0.0364
RT†	195 d	22.1	12.9	4.05	65.0	0.0370
RT	442 d	23.8	11.2	2.94	65.0	0.0326
90	22 h	20.8	27.2	3.00	52.0	0.0360
90	46 h	20.1	10.6	3.71	69.3	0.0380
90	70 h	19.9	6.1	4.31	74.0	0.0390
90	94 h	20.8	4.4	5.25	74.8	0.0428

† The 45, 60 and 75 °C solutions were further aged at room temperature after heating.

‡ "Mono", "rapid" and "slow" refer to monomeric Al ions and rapid- and slow-reacting polynuclear OH-Al complexes.

RESULTS AND DISCUSSION

The control solution initially contained 19, 79 and 2% of the total Al as monomeric ions and rapid- and slow-reacting complexes (Table 1). The degradation rate of the rapid-reacting complexes greatly increased with increased temperature (Table 1). Thus, the rapid-reacting complexes reduced to 75, 66, 35 and 6%, after 70 h of heating at 45, 60, 75 and 90 °C. The degradation of the rapid-reacting complexes followed first-order kinetics, as shown by the linear log (Al_{13}) against time plot (Figure 1) at each temperature level. The rate constants for the degradation at different temperatures were calculated to be 0.00044, 0.00129, 0.00467 and 0.01941 h^{-1} for the 45, 60, 75 and 90 °C solutions. The rate constant for the degradation of rapid-reacting complexes at room temperature was 0.000035 h^{-1} (Tsai and Hsu 1985). The decrease in the rapid-reacting complexes was accompanied by an increase in the slow-reacting complexes. The concentration of monomeric Al ions probably increased slightly with time, but the magnitudes of the changes were small and masked by the experimental uncertainty.

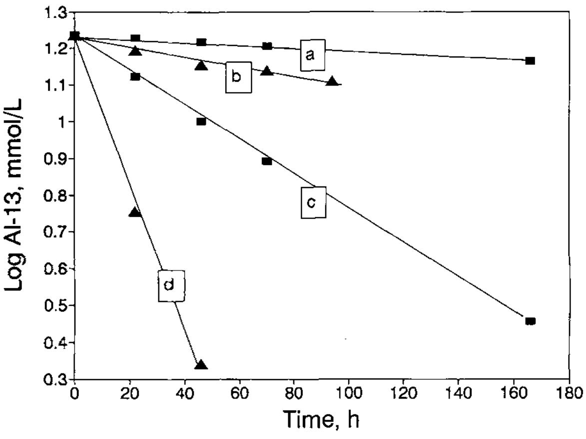

Figure 1. Kinetics of the degradation of Al_{13} complexes as a function of temperature: a) 45 °C; b) 60 °C; c) 75 °C; and d) 90 °C.

Table 2. Effect of temperature on the change in solution turbidity (FTU†) during heating.

Duration of heating, h	Temperature, °C			
	45	60	75	90
0	0.45	0.45	0.45	0.45
22	0.43	0.80	0.79	0.70
46	0.45	0.78	0.73	0.73
70	0.50	0.90	0.73	0.90
94	—	0.73	—	1.80
166	0.43	—	0.60	—

† FTU = formazine turbidity unit.

The turbidity of the solutions heated at 45, 60 or 75 °C for up to 166 h changed little, but that of the 90 °C solution increased slightly with time (Table 2). At the end of the experimentation (442 d at room temperature after heating), 20 mL of each solution were shaken with 2 g of Na-resin (AG 50 X8) for 1 h. The solution was filtered through a Whatman #42 filter paper to remove the resin. Only trace Al remained in solution after the resin treatment for the solutions heated at 45, 60 or 75 °C, and 18% of the Al remained in solution for the 90 °C solution. These results suggest that the slow-reacting components developed during heating were largely soluble species. A small amount of solid, however, was found in the 90 °C solution, which then became visibly turbid.

Hsu (1988) suggested that the Al_{13} degraded to either more stable complexes or $Al(OH)_3$ solid, depend-

Table 3. Effect of temperature on the change in solution pH during heating.

Duration of heating, h	Temperature, °C			
	45	60	75	90
0	4.22	4.22	4.22	4.22
22	4.17	4.15	4.07	3.98
46	4.16	4.15	4.06	3.55
70	4.21	4.15	4.00	3.59
94	—	4.10	—	3.26
166	4.19	—	3.92	—

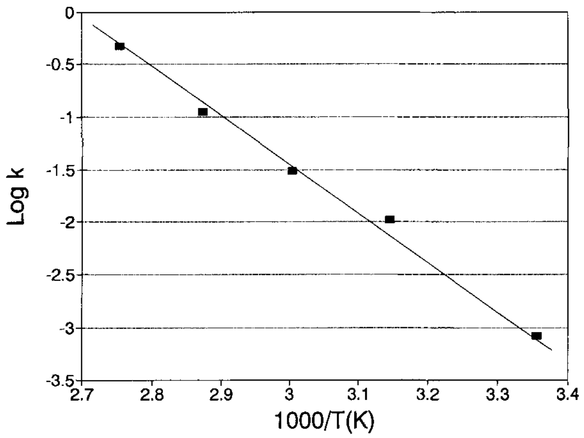

Figure 2. Dependence of Al_{13} degradation constant upon temperature. The room temperature degradation constant was taken from Tsai and Hsu (1985).

ing upon the absence or presence of nuclei. In the absence of nuclei, the Al_{13} complex rearranges its structure to form slow-reacting soluble species. In the presence of nuclei, the Al_{13} complex dissociates to release Al^{3+} ions to solution, which redeposit onto the nuclei to form $Al(OH)_3$ solid. The slow-reacting complex, once formed, changes to solid-phase $Al(OH)_3$ slowly, because of its resistance to reaction.

Table 3 shows that solution pH slightly decreased during aging at all temperature levels. Because the conversion of any polynuclear OH-Al complex to monomeric ions must be accompanied by a release of OH^- to solution, the decrease in pH must be attributed to the degradation of rapid- to slow-reacting complexes. Therefore, the slow-reacting complexes should be more basic than rapid-reacting complexes. The increased amount of OH^- associated with the slow-reacting OH-Al complexes, however, was small relative to the OH^- originally added in solution preparation. For example, the initial pH of the control OH-Al solution was pH 4.22, and it decreased to 3.92 after being heated at 75 °C for 166 h. This corresponds to an increase of 0.13 mmol H^+/L in solution, or the same amount of OH^- with the complexes. This increase corresponds to only 0.3% of the OH^- added in solution preparation (40 mmol OH^-/L). Therefore, the sulfate-induced precipitates from both rapid- and slow-reacting OH-Al complexes were not noticeably different in basicity (Tsai and Hsu 1985; Wang and Hsu 1994). The minor change in H^+ stoichiometry during aging also rules out solid $Al(OH)_3$ as the degradation product.

The plot of the logarithm of the degradation constants against the reciprocal of absolute temperature yielded a nearly straight line (Figure 2). The activation energy for the transformation calculated using the Arrhenius equation was found to be 84.9 kJ mol^{-1}. Turner (1976) reported similar results earlier and calculated the activation energy to be 76.7 kJ mol^{-1}.

When the 45, 60 and 75 °C solutions were further aged at room temperature, the transformation from rapid- to slow-reacting complexes continued to progress slowly, and the reaction was not reversible (Table 1). The 90 °C solution, after prolonged aging at room temperature, was not speciated because it became visibly turbid, and the Al-ferron color was not fully developed even after 7 d of reaction. This experiment thus provided additional evidence that the transformation of the Al_{13} complexes to the more stable $Al(OH)_3$-fragment structure is irreversible. Therefore, any model based upon the equilibrium between Al_{13} and monomeric Al^{3+} ions, such as Equation [1], is questionable:

$$13\ Al^{3+} + 32\ OH^- = [Al_{13}(OH)_{32}]^{7+} \qquad [1]$$

Most of the evidence for Al_{13} complexes was obtained from the study of fresh, laboratory-hydrolyzed OH-Al solutions. However, commercial OH-Al solutions, such as aluminum chlorohydrate and polyaluminum chloride, are employed in industries. These commercial OH-Al solutions contain only a small fraction of their Al as Al_{13} (Wang and Hsu 1994). Commercial aluminum chlorohydrates are prepared at 70 to 80 °C. The difference in preparation temperature probably accounts for the different distribution in polynuclear OH-Al complexes.

Kloprogge et al. (1992) prepared 3 OH/Al = 2.5 solutions at 25, 40 and 75 °C. They reported that the amounts of Al_{13} complex in these solutions increased from 52.0% for the 25 °C preparation to 80.6% for the 75 °C preparation. At the same time, the NMR undetectable species decreased from 43.6% at 25 °C to 13.8% at 75 °C. The discrepancy between their results and the present report was probably attributed to different experimental conditions. In the present study, the OH-Al solution was prepared by dropwise addition of NaOH to $AlCl_3$ solution. The localized alkalinity at the spot of NaOH introduction could pull Al^{3+} and OH^- ions together and help the formation of Al_{13} complex as well as $Al(OH)_3$ nuclei. However, the localized high alkalinity disappears after the solution homogenizes. Temperature probably affects both the initial localized high alkalinity effect and the subsequent degradation of Al_{13} complex. In the present study, the OH-Al solution was aged for 5 d at room temperature before the heating experiment. Therefore, only the effect of temperature on the degradation of Al_{13} complex was observed. In contrast, Kloprogge et al. (1992) prepared and analyzed their solutions at elevated temperature. Their results probably reflect the effects of temperature on both the initial localized high alkalinity and the degradation of Al_{13} complex. Furthermore, using the slow addition of NaOH at room temperature, the concentration of Al_{13} complexes could reach 91%

in an OH/Al = 2.5 solution 3 d after preparation (Wang and Hsu 1994).

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