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Determination of Ideal Broth Formulations Needed to Prepare Hydrous Aluminum Oxide Microspheres via the Internal Gelation Process

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DETERMINATION OF IDEAL BROTH FORMULATIONS NEEDED TO PREPARE HYDROUS ALUMINUM OXIDE MICROSPHERES VIA THE INTERNAL GELATION PROCESS

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ABSTRACT

A simple test-tube methodology was used to determine optimum process parameters for preparing hydrous aluminum oxide microspheres by the internal gelation process. Broth formulations of aluminum, hexamethylenetetramine, and urea were found that can be used to prepare hydrous aluminum oxide gel spheres in the temperature range of 60–90°C. A few gel-forming runs were made in which microspheres were prepared with some of these formulations in order to equate the test-tube gelation times with actual gelation times. These preparations confirmed that the test-tube methodology is reliable for determining the ideal broths.

1. INTRODUCTION

The internal gelation process is one of the sol-gel processes developed for the preparation of microspheres of hydrous metal oxides. In this process, chilled clear broth droplets containing the salt of the metal, hexamethylenetetramine (HMTA), and urea are heated, which causes homogenous gelation and solidification of the droplets.[1-14] After washing treatments, the gel spheres can be either air dried for use as engineered ion-exchange materials[7–11] or, depending upon the metal, dried, calcined, and sintered to ceramic microspheres for use as nuclear fuel,[1–6] catalysts,[7–11] getters,[7–10] or dielectrics.[12–14] A previously reported test-tube methodology,[15] which was employed to determine the optimum process parameters for preparing hydrous metal oxide microspheres, was also used in this study to determine the optimum process parameters for preparing hydrous aluminum oxide microspheres. The testing procedures are described in Appendixes A and B. The key to being able to prepare hydrous aluminum oxide gel spheres by this process depends upon an understanding of the behavior of aluminum in acidic and basic solutions. Hydrous aluminum oxide gels at a pH of ~4 in a nitrate or chloride solution. Aluminum hydroxide gels are amphoteric and will dissolve in an excess of either a strong acid or a strong base. If the solution becomes too basic (pH $\geq$10), the aluminum forms the hydroxide complex $(AlOH)_4^-$ and goes back into solution. Fortunately, in the internal gelation process, HMTA acts as a buffer, which keeps the gelling broth chemistry in the pH range of 4–7. To prevent the hydrous aluminum gel spheres from dissolving, the process chemistry has to be controlled in the allowable pH range. After gel spheres are formed, they have to be carefully washed. This study found the gel spheres could be washed with ammonium hydroxide (NH_4OH) solutions with a pH of $\leq$10 or $\leq$0.00005 *M* or with 0.001 *M* ammonium nitrate (NH_4NO_3) solutions with a pH of 6.1. The spheres could then be washed with deionized water to further remove any remaining impurities. At temperatures of 60–90^oC, which are used in the internal gelation process, the gelation of aluminum probably results in the formation of bohmite ($AlO(OH)_2$) gel spheres. However, before describing the experimental results, it is important to understand the basic chemical reactions of the internal gelation process.[4] The most important of these reactions are as follows:

(1) *complexation/decomplexation*

$$2CO(NH_2)_2 + Al^{3+} \leftrightarrow Al[CO(NH_2)_2]_2^{3+}$$

(2) *hydrolysis*

$$Al^{3+} + xH_2O \leftrightarrow AlO(OH)\bullet yH_2O_9 + 3H^+ \text{ and}$$
$$Al^{3+} + xH_2O \leftrightarrow Al(OH)_3\bullet yH_2O_9 + 3H^+$$

(3) *HMTA protonation*

$$(CH_2)_6N_4 + H^+ \leftrightarrow (CH_2)_6N_4\bullet H^+$$

(4) *HMTA decomposition*

$$(CH_2)_6N_4\bullet H^+ + 3H^+ + 6H_2O \leftrightarrow 4NH_4^+ + 6CH_2O.$$

Urea serves as a complexing agent for the metal (reaction 1). For broths of certain concentrations, the urea allows stable broths to be prepared at 0°C. As the temperature of the broth droplets rises after the droplets have been injected into the hot organic medium, decomplexation occurs (reaction 1), allowing hydrolysis of the aluminum to take place (reaction 2). HMTA, a weak organic base, drives the hydrolysis reaction to completion. At first the HMTA molecules are singularly protonated (reaction 3). Once most of the HMTA molecules (≥95%) are protonated, they begin to decompose (reaction 4) into ammonia molecules, which make the system even more basic. Each protonated HMTA molecule can effectively remove three additional hydrogen ions. The reaction products are formaldehyde and NH_4NO_3 or ammonium chloride. In addition to its role as a complexing agent, urea also functions as a catalytic agent, which accelerates the decomposition of the protonated HMTA molecules.[4]

2. PREPARATION OF STOCK SOLUTIONS

In preparing stock solutions for use in the internal gelation process, experience has shown it is generally best to make the stock solutions as concentrated as possible; however, supersaturated solutions should be avoided. When possible, stock solutions for any element to be gelled by this process should be partially neutralized with NH_4OH. By doing so, ideal broths for making gel spheres can be prepared with higher metal

concentrations and less HMTA. Generally the urea/metal mole ratio needs to be ≥1. In this study, five aluminum stock solutions of the following concentrations were prepared: (1) 2.335 *M* $Al(NO_3)_3$; (2) 2.164 *M* $Al(OH)_{0.5}(NO_3)_{2.5}$; (3) 2.017 *M* $Al(OH)_{1.0}(NO_3)_{2.0}$; (4) 1.888 *M* $Al(OH)_{1.5}(NO_3)_{1.5}$; and (5) 1.775 *M* $Al(OH)_{2.0}(NO_3)_{1.0}$. Partially neutralized aluminum stock solutions were prepared by slowly adding the necessary amount of chilled 14.8 *M* NH_4OH and deionized water to predetermined volumes of chilled 2.335 *M* $Al(NO_3)_3$ stock solution. After being added to the centrifuge tubes at ambient temperature, each solution was chilled to ice-bath temperature before being mixed together. The NH_4OH reagent had been recently purchased and hence was analyzed to confirm its molarity. The density of the NH_4OH was measured as 0.904 g/mL, and the exact volume of NH_4OH was obtained by weighing it on an analytical balance. A stock solution (3.17 *M* HMTA and 3.17 *M* urea) with a density of 1.14 g/mL was prepared. In using these stock solutions to prepare clear broths, long mixing times were needed for the broths with OH^-/Al^{3+} mole ratios of >1. To shorten the mixing time of these broths, HMTA-urea stock solutions were also prepared with higher urea concentrations and lower HMTA concentrations, which allowed the urea/Al^{3+} mole ratios of these broths to be ≥1.

3. EXPERIMENTAL RESULTS

Optimum broth formulations and gel-forming temperatures were determined for making structurally strong hydrous aluminum oxide microspheres via the internal gelation process. One of the most critical factors in the formation of the gel spheres is the time required for broth droplets to gel once they are introduced into the hot immiscible organic medium in the forming column. Ideally, gelation should begin in ≤10 s.

Numerous test-tube experiments were conducted with broths prepared using stock solutions to determine which broth formulations at 60, 70, 80, and 90°C had gel times ≤10 s and had good gel characteristics. The concentrations of Al^{3+} in broths with OH^-/Al^{3+} mole ratios of 0.00, 0.50, 1.00, 1.50, and 2.00 are given for different HMTA/Al^{3+} mole ratios in Table 1. All the broths given in Table 1 were clear and stable. A stable broth is one that remains clear and does not gel or precipitate within 1 h at 0°C.

Table 1. Concentration of Al^{3+} in the broths used in this study for the indicated OH^-/Al^{3+} and $HMTA/Al^{3+}$ mole ratios

OH^-/Al^{3+} (mole ratio)	$HMTA/Al^{3+}$ (mole ratio)	Al^{3+} concentration in broth (*M*)
0.00	2.8	0.767
0.00	2.6	0.806
0.00	2.4	0.849
0.00	2.2	0.896
0.00	2.0	0.949
0.00	1.8	1.009
0.00	1.6	1.155
0.50	2.8	0.748
0.50	2.6	0.785
0.50	2.4	0.825
0.50	2.2	0.870
0.50	2.0	0.920
0.50	1.8	0.976
0.50	1.6	1.039
1.00	1.2	1.480
1.00	1.1	1.190
1.00	1.0	1.237
1.00	0.9	1.287
1.00	0.8	1.341
1.00	0.7	1.399
1.00	0.6	1.463
1.00	0.5	1.534
1.50	0.9	1.233
1.50	0.8	1.283
1.50	0.7	1.336
1.50	0.6	1.394
2.00	0.5	1.390
2.00	0.4	1.453
2.00	0.3	1.522
2.00	0.2	1.598
2.00	0.1	1.682

The speed at which a clear broth is formed after the chilled stock solutions are mixed is also important. Broths that were prepared from solutions in which the urea/Al^{3+} mole ratio was <1 took much longer to clear, in some cases up to an hour. For a broth to clear quickly (≤5 min), the HMTA-urea stock solution had to be modified accordingly by increasing the urea concentration and decreasing the HMTA concentration. The urea/Al^{3+} mole ratio in a broth needs to be ≥1. The results of test-tube experiments conducted using broths prepared from a stock solution of 3.17 *M* HMTA and 3.17 *M* urea are given in Figs. 1–11. In Figs. 1–5, the gelation time is shown as a function of HMTA/Al^{3+} mole ratio for Al^{3+} broths at 90, 80, 70, and 60°C. These data show that as the OH^-/Al^{3+} mole ratio increases from 0.00 to 2.00, less HMTA is needed for the broth formulations, which gel in ≤10 s at each temperature tested. Also, as the temperature increases, even less HMTA is needed. These data provide the user with a large number of formulations which can be used to prepare hydrous aluminum oxide gel spheres. Considering the economics of gel-forming operations, broth formulations with lower gel-forming temperatures of 60–70°C are best. At these temperatures, trichloroethylene (TCE) can be used as the immiscible gel-forming medium rather than silicone oil, thus eliminating a washing step. Also, to minimize the use of HMTA at the lower gel-forming temperatures, broths with higher OH^-/Al^{3+} mole ratios can be used. These trends are shown in Figs. 6–9 in which gelation time is given as a function of HMTA/Al^{3+} and OH^-/Al^{3+} mole ratios for broths that had gel times of 5 and 10 s at gel-forming temperature of 90, 80, 70, and 60°C, respectively. These plots, as well as those in Figs. 10 and 11, allow the user to pick an ideal broth that best suits the needs of his/her application. For example, broth droplets that gel in 5 s are less likely to coalesce in small-diameter, lab-scale, gel-forming columns such as those described in detail in Refs. 5 and 10, which are more commonly used. In larger-scale gel-forming production columns in which the flow of the immiscible organic is more laminar, somewhat higher gelation times can be employed. All of the broth formulations tested with gelation times of ≤10 s produced good microspheres with firm structure. In the test-tube experiments, the gels were aged for 10 min and cooled to ambient temperature. The rigidity and pH of the gels were then measured as described in Appendix B. The pH of the aged gels was

generally >4.9, with most in the range of 5 to 5.4, which indicated the completeness of gelation. It was also experimentally found that the gel spheres needed to be aged for 15–20 min and at the lower temperatures (60–70°C). Figures 1–5 give rigidity values for many of the data points. The values range from 1 to 7 on a scale of 1 to 10 with 1 being very fluid-like water and 10 being very hard. Most of the gels which formed in ≤10 s at 60 or 70°C were in the range of 4 to 5. These gels had OH^-/Al^{3+} mole ratios of ≤1. None of the broths with OH^-/Al^{3+} mole ratios of 1.5 or 2.0 gelled in ≤10 s, so if these broths were to be used, they would have to be gelled at 80 or 90°C. Similarly, their rigidities were in the range of 4.5 to 5.5. Some of the broths with gelation times of 10 s or less formed gels with values as high as 7. Ones with a rigidity value of 1 did not gel completely.

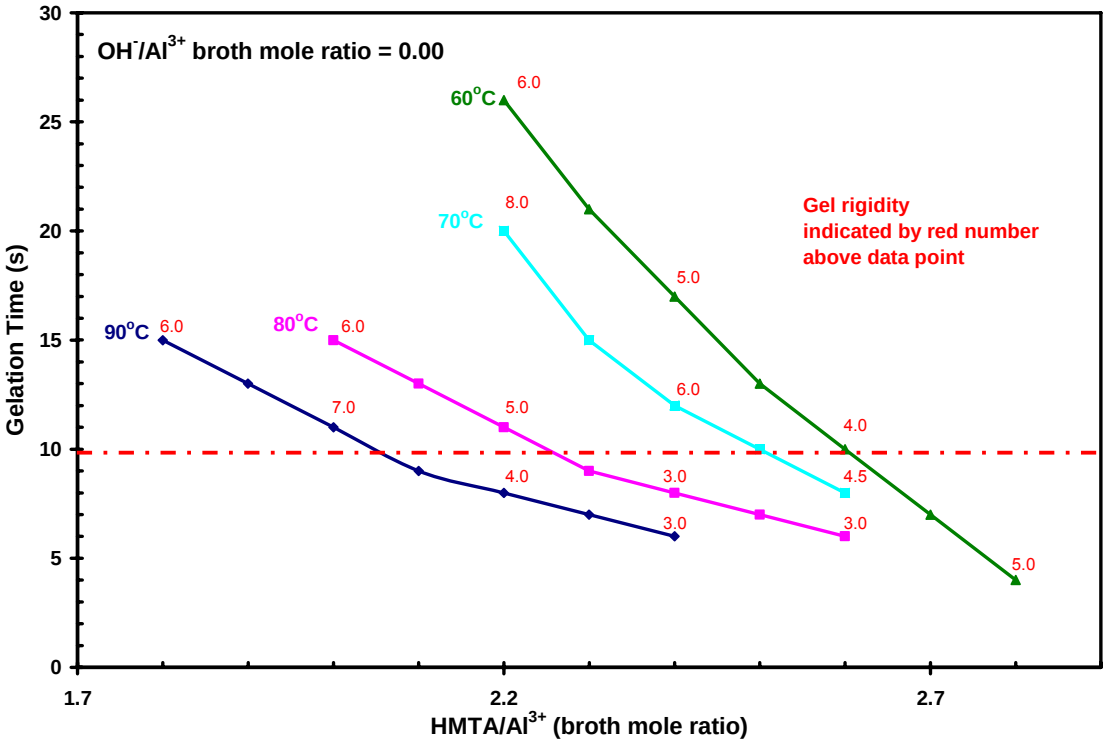

Fig. 1. Gelation time as a function of $HMTA/Al^{3+}$ mole ratio for Al^{3+} broths at 90, 80, 70, and 60°C with a OH^-/Al^{3+} mole ratio of 0.00.

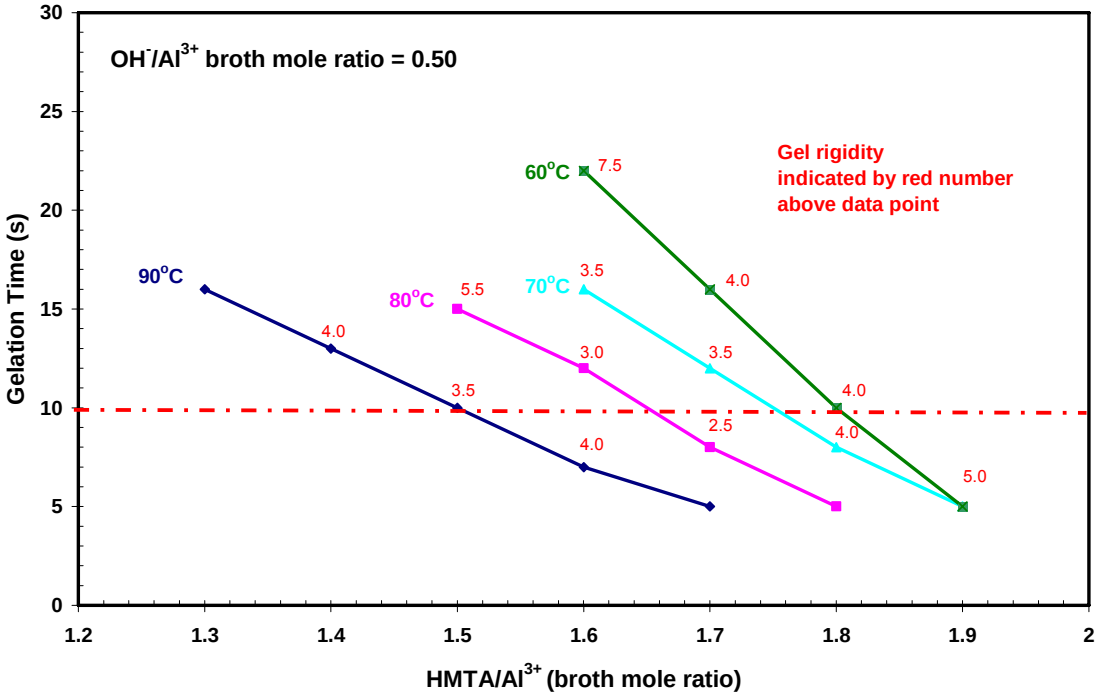

Fig. 2. Gelation time as a function of HMTA/Al^{3+} mole ratio for Al^{3+} broths at 90, 80, 70, and 60°C with a OH^{-}/Al^{3+} mole ratio of 0.50.

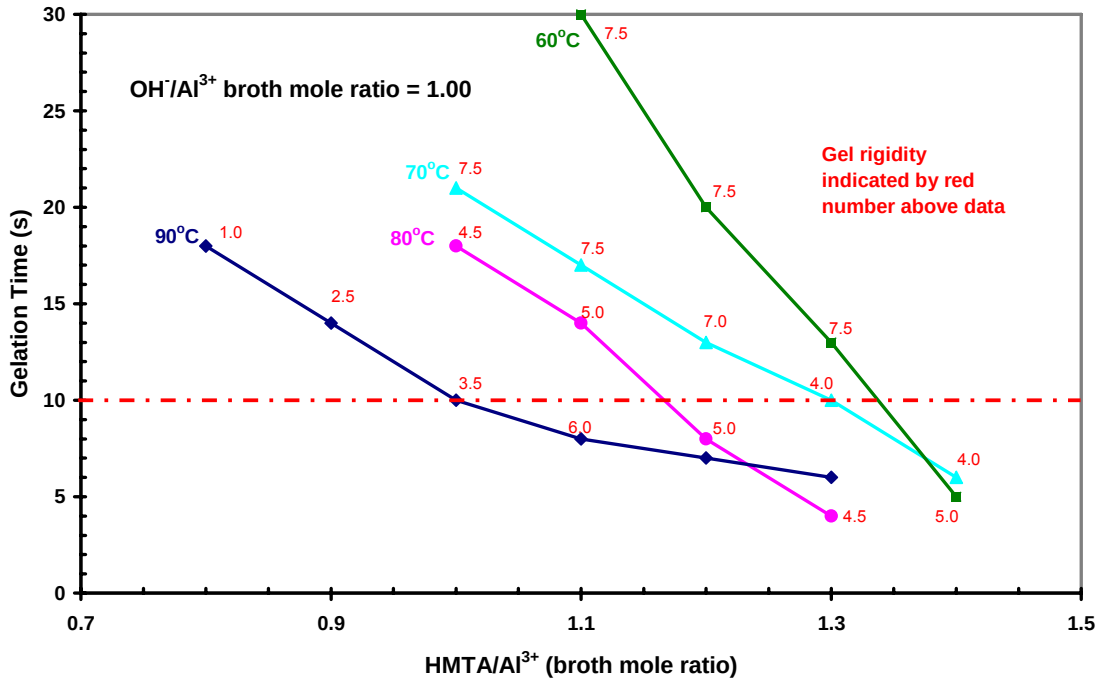

Fig. 3. Gelation time as a function of HMTA/Al^{3+} mole ratio for Al^{3+} broths at 90, 80, 70, and 60°C with a OH^{-}/Al^{3+} mole ratio of 1.00.

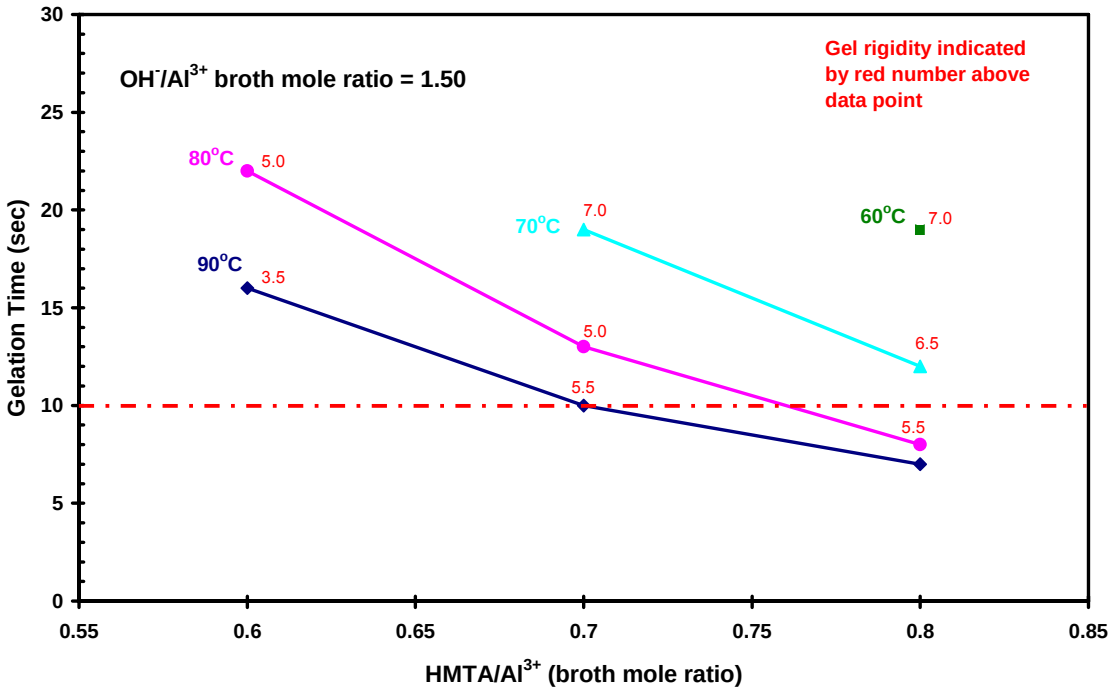

Fig. 4. Gelation time as a function of HMTA/Al^{3+} mole ratio for Al^{3+} broths at 90, 80, 70, and 60°C with a OH^{-}/Al^{3+} mole ratio of 1.50.

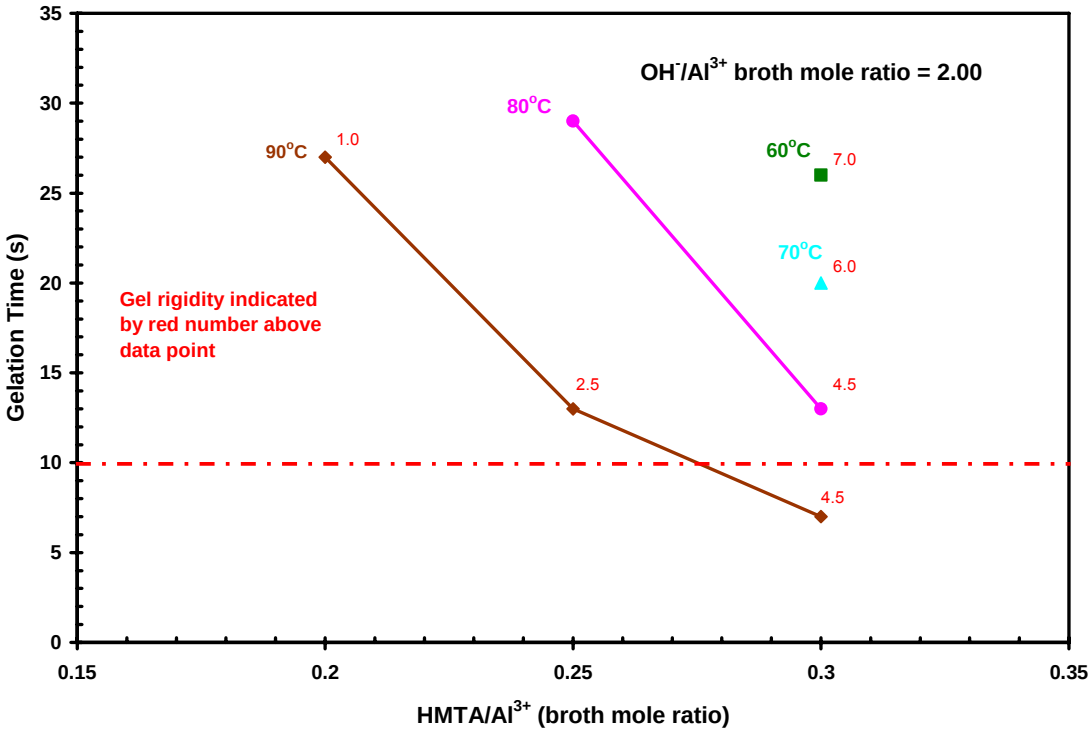

Fig. 5. Gelation time as a function of HMTA/Al^{3+} mole ratio for Al^{3+} broths at 90, 80, 70, and 60°C with a OH^{-}/Al^{3+} mole ratio of 2.00.

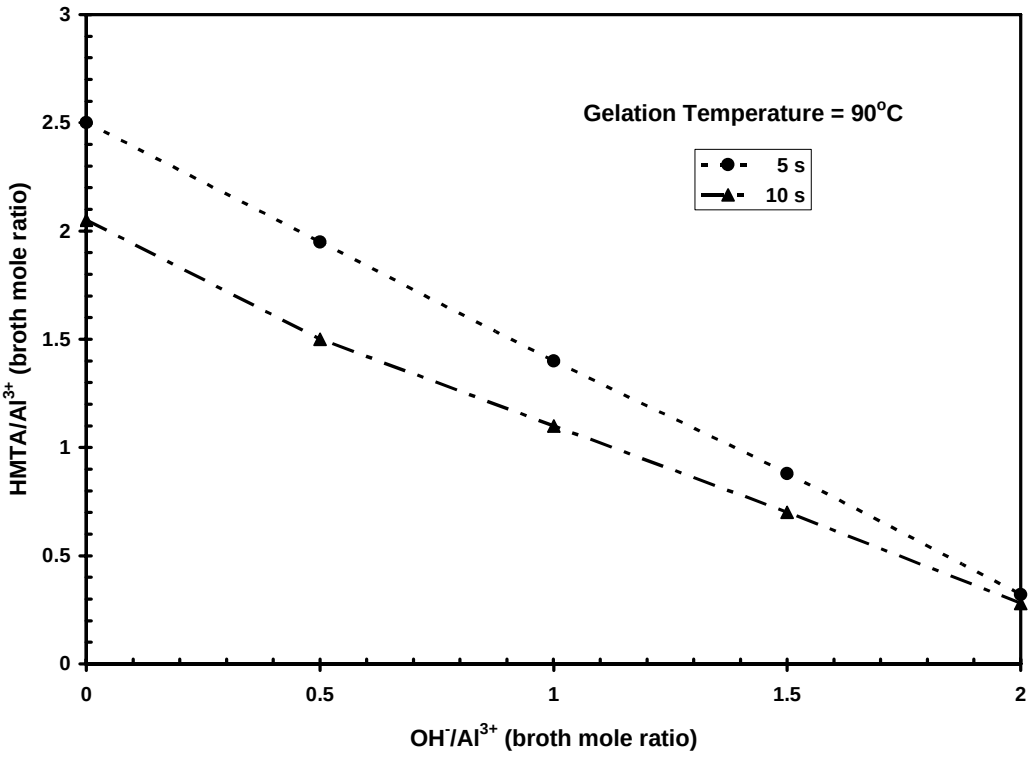

Fig. 6. Ideal Al^{3+} broths which gel at 90°C in 5 and 10 s as a function of HMTA/Al^{3+} and OH^-/Al^{3+} mole ratios.

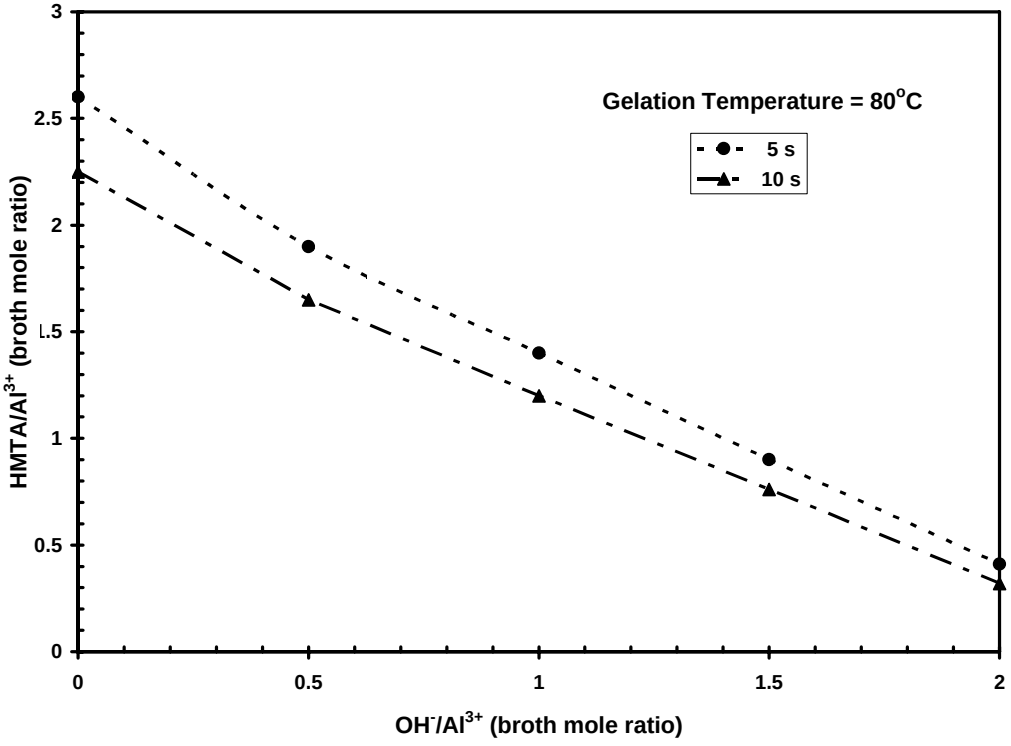

Fig. 7. Ideal Al^{3+} broths which gel at 80°C in 5 and 10 s as a function of HMTA/Al^{3+} and OH^-/Al^{3+} mole ratios.

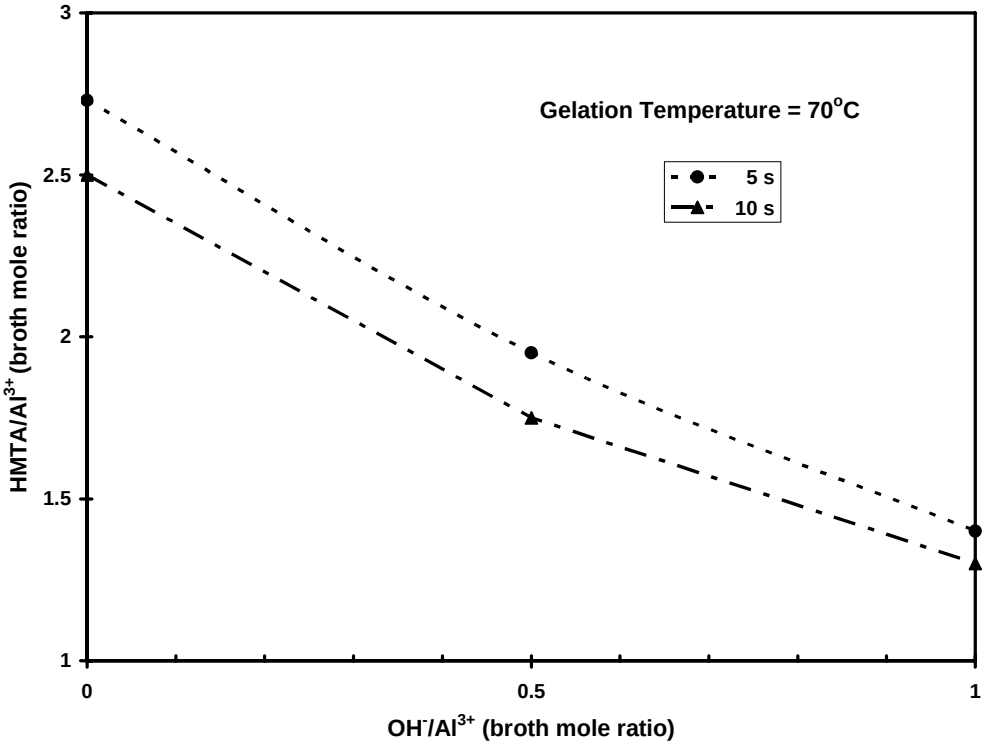

Fig. 8. Ideal Al^{3+} broths which gel at 70°C in 5 and 10 s as a function of HMTA/Al^{3+} and OH^{-}/Al^{3+} mole ratios.

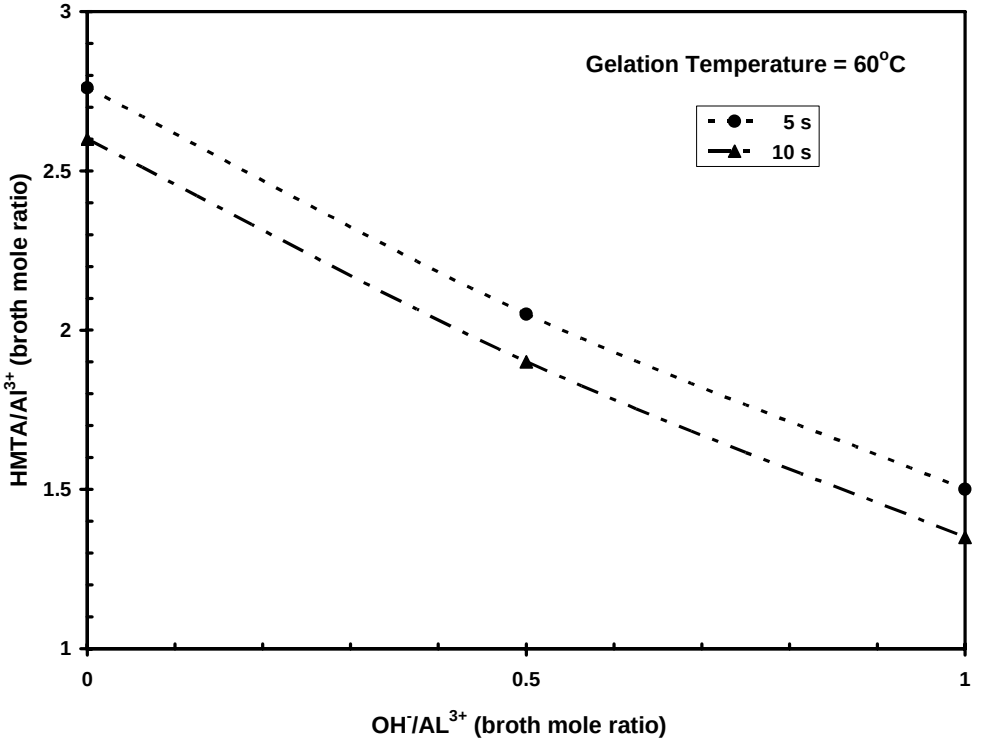

Fig. 9. Ideal Al^{3+} broths which gel at 60°C in 5 and 10 s as a function of HMTA/Al^{3+} and OH^{-}/Al^{3+} mole ratios.

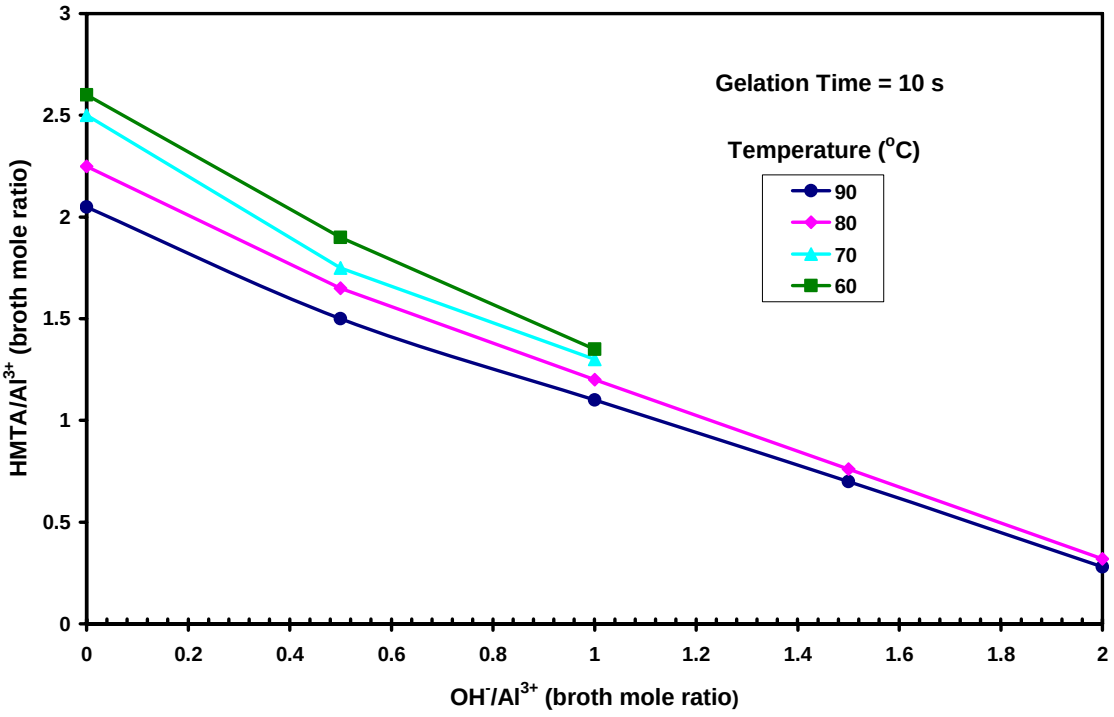

Fig. 10. Ideal Al^{3+} broths which gel in 10 s as a function of HMTA/Al^{3+} and OH^{-}/Al^{3+} mole ratios at 90, 80, 70 and 60°C.

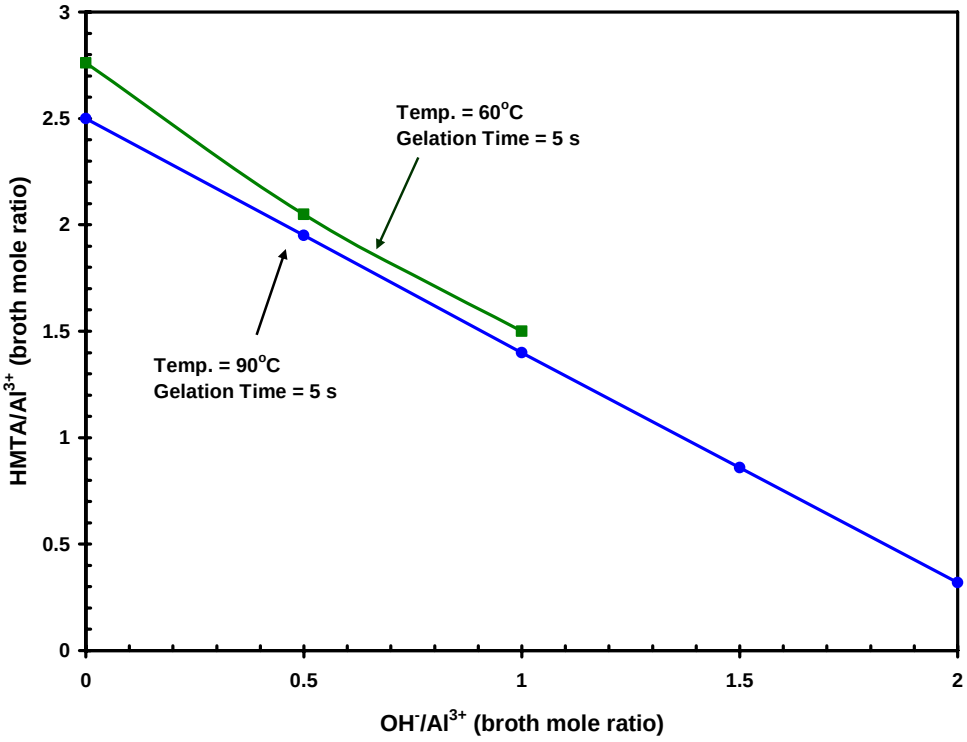

Fig. 11. Zone for ideal Al^{3+} broths which gel in 5 s as a function of HMTA/Al^{3+} and OH^{-}/Al^{3+} mole ratios at 60 and 90°C.

As previously described, a broth formulation with a OH^-/Al^{3+} mole ratio of ≥1 cleared quickly when the chilled stock solutions were mixed if the urea/Al^{3+} mole ratio was ≥1. Several broths were prepared in this study in which the concentrations of HMTA and urea were varied. By increasing the concentration of urea, the concentration of HMTA had to be decreased to provide a clear, saturated stock solution. One of the stock solutions was prepared using 2.5 *M* HMTA and 4.7 *M* urea. A 1.18 *M* Al^{3+} broth was prepared with it which had OH^-/Al^{3+}, HMTA/Al^{3+}, and urea/Al^{3+} mole ratios of 1.5, 0.8, and 1.5, respectively. The broth was clear after being mixed for 4.5 min., and its gelation time at 80°C was ~9 s. The rigidity value was 6 after 10 min of aging. A comparable 1.28 *M* Al^{3+} broth with OH^-/Al^{3+}, HMTA/Al^{3+}, urea/Al^{3+} mole ratios of 1.5, 0.8, and 0.8, respectively, took ~15 min to clear when the chilled stock solutions were mixed. The standard stock solution (3.17 *M* HMTA and 3.17 *M* urea) was used to prepare this broth. This broth also gelled at 80°C in ~9 s and had a rigidity value about 5.5 after 10 min of aging. In another broth with identical OH^-/Al^{3+} and HMTA/Al^{3+} mole ratios but with a urea/Al^{3+} mole ratio of 1.28, the broth cleared in 5 min, gelled in ~9 s, and had a rigidity value of ~5.5 after 10 min of aging. Numerous other tests were also conducted which demonstrated that the urea/Al^{3+} mole ratio of a broth must always be ≥1 to ensure that the broth quickly clears of gel solids when the chilled stock solutions are mixed.

4. AN EXAMPLE OF ONE OF THE LAB-SCALE PREPARATIONS OF HYDROUS ALUMINUM OXIDE MICROSPHERES

A 123.2 mL broth was prepared by slowly mixing 73.2 mL of chilled 3.19 *M* HMTA and 3.19 *M* urea solution (0–5°C) with 50 mL of chilled 2.335 *M* aluminum nitrate stock solution prepared with a OH^-/Al^{3+} mole ratio of 0.00. The HMTA/Al^{3+} and urea/Al^{3+} mole ratios were 2.0. The concentrations of Al^{3+}, HMTA, and urea for the broth were 0.95, 1.9, and 1.9 *M,* respectively. A two-fluid nozzle system with a 21 gauge flat-tipped needle was used to provide the broth droplets.[10] From the tip of the needle, the broth droplets were introduced into a flowing stream of heated immiscible organic medium (~90°C). Silicone oil (Dow Corning 200 silicone fluid) was used in this preparation. The droplets were then transported into the gel-forming apparatus. The size of the droplets could be controlled by using a two-fluid nozzle concept and varying the

gauge of the needle and the flow rates of the hot silicone oil and the chilled broth. The droplets began to gel in 10–11 s and were subsequently collected in a stainless steel mesh basket downstream. It took ~30 s for the gelled microspheres to reach the basket, and the run lasted ~40 min. Afterward, the microspheres were aged for 20 min in silicone oil at ~80°C to complete the gelation process, washed six times with TCE to remove the silicone oil, and then washed six times with 0.00005 *M* NH_4OH (pH = 9.5) to remove the reaction impurities. The bead volume after the washing steps was ~158 mL. If these beads had been dried, calcined, and sintered, about 10.3 g Al_2O_3 of beads theoretically could have been produced if 100% recovery were possible. The theoretical density of Al_2O_3 was 3.97 g/mL, and the measured tap density of the air-dried aluminum microspheres was 1.02 g/mL. The run was a success, and the gel time was about the same as that predicted by the test-tube experiments. Figure 12 provides a 10× microscopic image of a sample of the air-dried hydrous aluminum oxide microspheres that were prepared. The diameters of the microspheres prepared in this run were in the range of 400 to 799 μm.

Fig. 12. A 10× microscopic image of a sample of hydrous aluminum oxide microspheres which were air dried at ambient temperature.

5. ACKNOWLEDGMENTS

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APPENDIX A

BROTH STABILITY TESTS

A stable broth is one that remains clear and does not gel or precipitate for reasonable periods of time at ~0°C (usually about 1 h). Five aluminum stock solutions of the following concentrations were prepared: (1) 2.335 *M* $Al(NO_3)_3$; (2) 2.164 *M* $Al(OH)_{0.5}(NO_3)_{2.5}$; (3) 2.017 *M* $Al(OH)_{1.0}(NO_3)_{2.0}$; (4) 1.888 *M* $Al(OH)_{1.5}(NO_3)_{1.5;}$ and (5) 1.775 *M* $Al(OH)_{2.0}(NO_3)_{1.0}$. The partially neutralized aluminum stock solutions were prepared by slowly adding chilled 14.8 *M* NH_4OH and deionized water to predetermined volumes of chilled 2.335 *M* $Al(NO_3)_3$ stock solution. Each solution was chilled to ice-bath temperature. The NH_4OH reagent had been recently purchased and hence was analyzed to confirm its molarity. A stock solution (3.17 *M* HMTA and 3.17 *M* urea) with a density of 1.14 g/mL was prepared. The stability test procedure was as follows.

1. A rack for holding thin-walled glass centrifuge tubes was placed in an ice bath. (Plastic tubes were not used because glass provides faster heat transfer.) Predetermined volumes of 3.17 *M* HMTA/3.17 *M* urea and aluminum stock solutions were separately and carefully pipetted into these tubes via calibrated electronic pipettes, and the tubes were subsequently chilled for ~20 min. The centrifuge tubes containing the aluminum stock solutions also served as the broth tubes and were labeled accordingly as to the stock solution that was used and the HMTA/Al^{3+} and OH^-/Al^{3+} mole ratios. Unless stated otherwise, the urea/Al^{3+} mole ratio was equal to the HMTA/Al^{3+} mole ratio.

2. To prepare a broth, a predetermined volume of chilled HMTA/urea was carefully removed with a pipette and transferred to a centrifuge tube containing a predetermined volume of aluminum stock solution. Because of the small volumes involved, it was important that the transfer was complete. The broth was then mixed well with a Teflon stirring rod without splashing any up on the surfaces of the test tube. The time of mixing was recorded, and the broth was observed until the first sign of gelation appeared, or for 1 h. The time of gelation was then recorded. Tests were performed in duplicate.

APPENDIX B

GEL TESTS IN GLASS CENTRIFUGE TUBES

Apparatus

The apparatus used for the gel tests was simple and consisted of the following components:

- 2-L beaker containing ice water
- 4-L beaker containing heated water
- hot plate with stirring capability
- stainless steel dial thermometer
- calibrated Metler DE 200 analytical balance (0- to 200-g range with a readability of 0.0001 g)
- calibrated continuously adjustable digital pipette (100- to 1000-µL range) or a calibrated Rainin EDP-Plus electronic pipette with interchangeable liquid ends that cover the 100- to 1000-µL and 250- to 2500-µL ranges, plus the concomitant disposable polyethylene tips
- ROSS™ Sure-Flow combination pH electrode, which provides temperature compensation for temperatures in the 0–100°C range
- in-date standard pH 7 and pH 4 buffer solutions
- 15-mL polypropylene centrifuge tubes with conical bottoms
- 15-mL glass centrifuge tubes with conical bottoms
- 8-in.-long Teflon-coated microspatulas

Testing Procedure

The gel test procedure was as follows.

1. A predetermined volume of an aluminum stock solution (at room temperature) was carefully pipetted into the bottom of a glass centrifuge tube and placed in an ice bath. The required volume of HMTA/urea (at room temperature) was pipetted into the bottom of a separate polypropylene centrifuge tube and placed in an ice bath. Both were chilled for 10 min to attain ice-bath temperature. The chilled HMTA/urea was then

quantitatively and slowly pipetted into the chilled aluminum solution and mixed well. Care was taken not to splash the broth onto the walls of the test tube. The broth was maintained in the ice bath for an additional 5 min.

2. The broth tube was then placed in a hot water bath at the desired temperature. The test tube was gently swirled in the water bath to observe when the gel set. A stopwatch was used to measure the time in the bath needed for gelation to occur. As gelation began, the clear broth became viscous and motionless. The gel was then allowed to age for 10 min in the hot bath at the same temperature.

3. The test tube was then removed from the hot bath, and the gel was allowed to cool to room temperature. The transparency of the gel on a scale of 1 to 10 with 1 being transparent, 4 being translucent, 7 being opaque, and to 10 being crystalline white was subjectively determined and recorded. The rigidity of the gel was subjectively determined by inserting a spatula into the center of the gel and was quantified on a subjective scale of 1 (no resistance, almost like water) to 10 (high resistance, difficult to penetrate). Any variation in color was also noted.

4. The gel was then broken up by stirring with the spatula, and the test tube was centrifuged to remove pockets of air and to compact the gel into the bottom of the tube. A calibrated pH probe was inserted into the gel to measure the pH. It took up to 30 s for the pH reading to stabilize.

At a minimum, duplicates of each broth were tested to ensure accuracy. If the gel times and properties matched, the test results were assumed to be valid. If the gel times did not match, additional tests were conducted to resolve the problem and obtain consistent values.