

Analysis of Pentasodium Triphosphate Hydration Kinetics

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The present work analyzes the effect of various factors on the hydration of pentasodium triphosphate. The experimental method is based on application of the hydration test. Technical-quality products with different proportions of phase I and phase II have been used. The variables studied are phase I/phase II ratio, initial temperature, particle size, stirring rate and composition of the slurry (presence of hexahydrate crystals and water hardness). The results have been discussed according to a kinetics model that includes a series of stages of a physical nature (dissolution of anhydrous salt and the crystallization of the hexahydrate), as well as of a chemical nature (solvation of the ions in solution). Crystallization of the hexahydrate may be the controlling stage in the process.

KEY WORDS: Builder, crystallization, detergent, eutrophication, hydration, pentasodium hexahydrated triphosphate, pentasodium triphosphate, pentasodium triphosphate hydration, slurry, washing powders.

Properties of detergents depend on the concentration of Ca^{++} and Mg^{++} ions in the washing medium (1,2). The effect of these ions can be reduced by sequestration or precipitation. Hence, a product that acts as a builder must be included in the detergent. Classically, the most widely used builder is pentasodium triphosphate (TPP), which appears in two crystalline anhydrous forms, phase I and phase II (3-5).

The influence that TPP exerts on the spray-drying process used in manufacturing washing powders is of great importance. The starting point for this process is an aqueous slurry in which a reaction between TPP and water occurs, giving rise to hexahydrated TPP (3-5).

The use of TPP in detergents presents some technical problems in industrial plants where their slurries are processed because of hydration of TPP in the bulk suspension. Each molecule of TPP reacts with six molecules of water to form a product with low solubility, hexahydrated TPP. This hydration, which has been extensively studied by several authors (6-9), takes place during the mixing operation and causes a considerable increase in the consistency of the slurry. Moreover, control of this stage is important because it may influence both production efficiency and detergent properties. Hence, before being injected into the spray-drying tower, the slurry must have specific and invariable properties.

In spite of the many advantages of TPP-containing detergents, there are also some problems that tend to limit the use of TPP. Thus, most industrialized countries have legal or volunteer programs to restrict or even forbid the use of TPP in detergents, because of ecological problems related to the eutrophication of lakes and other bodies of water.

To alleviate these problems, industries should concentrate their efforts on the following solutions: (i) A search of possible partial or total substitutes for TPP. (ii) Control of the

manufacturing process, which could be oriented toward a double objective: (a) the amount of phosphorus authorized in the final product must be in its optimum form, that is, hexahydrated TPP. To achieve this, further study of TPP hydration and the effects that potential substitutes may have on this process is needed; and (b) the detergent slurries containing TPP must be characterized rheologically and compared to those formulations in which TPP can be substituted for other builders.

The present paper is part of a research project in which the influence exerted by partial or complete replacement of TPP by other builders on the kinetics of TPP hydration and on the rheological properties of detergent slurries is being studied. Previous articles have discussed the changes in the rheological consistency of these slurries during the hydration process (10) or have dealt with the influence of some variables of technical interest on the rheological properties of slurries at steady state (11,12), or even under the influence of tartrate (replacement of TPP) (13), or zeolite and zeolite-citrate mixtures (14,15).

The present contribution focuses on the influence that relationship between phase I and phase II, initial temperature, particle size, stirring rate and slurry composition exert on TPP hydration. The proposed objective here is to establish the basis for further study of the influence that partial or total substitution of TPP by other builders has on the process.

EXPERIMENTAL PROCEDURES

Materials and methods. Of the existing methods used to control TPP hydration, we selected the so-called "Test of Hydration". The experimental method is a simplification of the DTA (Differential Thermal Analysis) technique (6). Its use is justified by the advantages offered—it provides sufficient information on TPP hydration, the thermal changes produced during that process are clearly detected, and it is easy to carry out. It is widely used at the industrial level for the routine control of product hydration. Moreover, by reducing the number of substances present in the reaction medium, interpretation of the results is facilitated.

The experimental procedure consists of recording temperature increase over time after the addition of 150 g of TPP to a solution containing 50 g of Na_2SO_4 in 200 g of water. The process is performed under practically adiabatical conditions and with sufficient agitation for the system to be isotropic.

Through a heat balance equation, the increase in temperature observed during the reaction can be related to the conversion of TPP. The heat generated by the reaction is equated to the heat given by the system plus that provided by the medium:

$$-N_0\Delta H_r \frac{dX_A}{d\theta} = C_p \frac{d(T-T_0)}{d\theta} + Q_{\text{transmitted}} \quad [1]$$

where N_0 is the initial of moles of TPP, ΔH_r the heat produced by TPP hydration at the initial temperature

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(cal/mole). C_p is the average calorific capacity of the container and its contents (cal/mole/°C). T_0 the initial temperature of the test (°C), T the temperature of the system (°C) after a given time, θ in min, and X_a is the conversion of TPP over a given time, θ . However, the impossibility of quantifying the amount of calorific losses in the experimental device used makes it impossible to explicitly establish the proposed relationship, at least during the complete period of hydration of the product. Therefore, the analysis and interpretation of the results are carried out on the basis of temperature measurements or the increase of temperature *vs.* the reaction time.

The experimental device consisted of a 0.5-L Dewar glass, tightly closed, with two holes located in the upper portion, through which a thermocouple and a stirrer with a shaped double-flap ending were introduced. The stirring rate was maintained at 650 rpm. The thermocouple was connected to a recorder.

Characteristics of the products used. Three types of product of technical grade (94–96% TPP, 56.6% P_2O_5 on dry base) with different phase I/phase II ratios were used. These products were analyzed to determine their water content, their phase I/phase II ratio and their particle size. The water content was established according to UNE procedure 55-543 (II) (part of ASTM Standard D820). The results obtained are shown in Table 1.

The content in phase I was determined by the test of temperature increase (16), adapting all the required precautions regarding the concentration of sodium pyrophosphate, size and water content (17). The average values obtained for each product are shown in Table 1 as well as those of the mean deviation (S) of the content in phase I (for the three measurements made).

Particle size was determined by sieving with an electromagnetic vibrator and ASTM serial sieves ranging from 0.59 and 0.025 mm. The results obtained are included in Table 1, along with the mean deviation of the 15 measurements made.

RESULTS

Influence of temperature and the phase I/phase II ratio. Analysis of the experimental results obtained (Fig. 1) shows that: (i) the influence of the initial temperature and, consequently, the temperature at which the process takes place, depends on the phase I/phase II ratio; (ii) temperature has a significant influence on TPP hydration. For example, in products with a higher content of phase I (TPP-A) an increase in temperature decreased TPP hydration, whereas in products with a higher content of phase II (TPP-B and TPP-C), temperature changes during the reaction are characterized by a period of induction. A temperature increase produces an increase in the induction period and a decrease in TPP hydration. Consequently, by increasing the content of phase II in the product, the TPP hydration rate is lessened.

Influence of particle size. This study was performed with the different fractions from the analysis of TPP particle size (Table 1). The influence of particle size on TPP hydration is shown in Figure 2. From the results obtained with TPP-A and TPP-B products, there does not appear to be a significant influence of particle size on product hydration. However, a decrease in particle size in the TPP-

TABLE 1

Characteristics of the Products Used^a

	TPP-A		TPP-B		TPP-C ^b	
	Weight	S (%)	Weight	S (%)	Weight	S (%)
Water content (%)	0.32		0.21		0.23	
Phase I (%) / mean deviation (%) ^c	24.6:0.3		12.1:0.5		1.0:1.4	
Size	Weight	S (%)	Weight	S (%)	Weight	S (%)
Greater than						
0.59/mm	0.2	0	0.1	0	0.4	0.1
0.59:0.125 mm	18.8	0.2	—	—	18.2	0.8
0.59:0.063 mm	—	—	27.0	0.7	—	—
0.125:0.053 mm	21.6	1.1	—	—	23.3	1.0
0.063:0.040 mm	—	—	15.1	2.5	—	—
0.053:0.040 mm	24.9	2.4	—	—	—	—
Sifting 0.053 mm	—	—	—	—	57.5	1.8
Sifting 0.040 mm	39.7	2.3	56.8	2.8	—	—

^aTPP, pentasodium triphosphate.

^bTPP-C was obtained by partial hydration of TPP-B.

^cMean deviation designated by "S".

B product produced a reduction in the induction period. In the TPP-C product, a decrease in particle size produced an increase in the initial rate of hydration and a reduction in the induction period.

Influence of stirring rate. Stirring of the slurry is an important factor in the hydration process because of the tendency of TPP and of the hexahydrate to precipitate and form clusters under the prevailing reaction conditions. Our previous experiments have shown that the slurry acquires a homogeneous appearance when the rate of stirring is higher than 400 rpm. During the hydration of TPP, the slurry was stirred at 450, 650, 850, 1000, 1200 or 1400 rpm. The study of the influence of stirring rate on TPP hydration is based on the results shown in Figure 3. When the stirring rate in the product with a higher content of phase I (TPP-A) was increased, the initial temperature gradient increased without significantly affecting the global rate of TPP hydration.

In products with a higher content of phase II (TPP-B and TPP-C), increased stirring led to an increase in the global rate of TPP hydration and a decrease in maximum temperature. No significant influence of stirring rate on the initial temperature gradient was observed. TPP hydration is more sensitive to stirring rate as particle size increases, as can be seen in Figure 4.

Influence of addition of hexahydrate crystals. This variable was studied because TPP is unstable in water, and when it is added to the slurry it can be partially hydrated, depending on the time of its storage. Moreover, as a consequence of the ecological problems caused by detergent systems containing phosphorus, the degree of hydrolysis of TPP has acquired importance. Various alternatives have been offered to solve these problems. One of them is based on the utilization of partially hydrated products (8,18).

The experiments were performed with the product with the highest content of phase II (TPP-B). Different quantities of hexahydrate crystals were added to a constant weight of product to produce the following percentages of total weight: 2, 4, 8, 10, and 15%. The hexahydrate crystals were prepared by the method recommended by Van Wazer (3–5) and Quimby (19).

The influence of added hexahydrate crystals on TPP hydration is shown in Figure 5. From these results it can be

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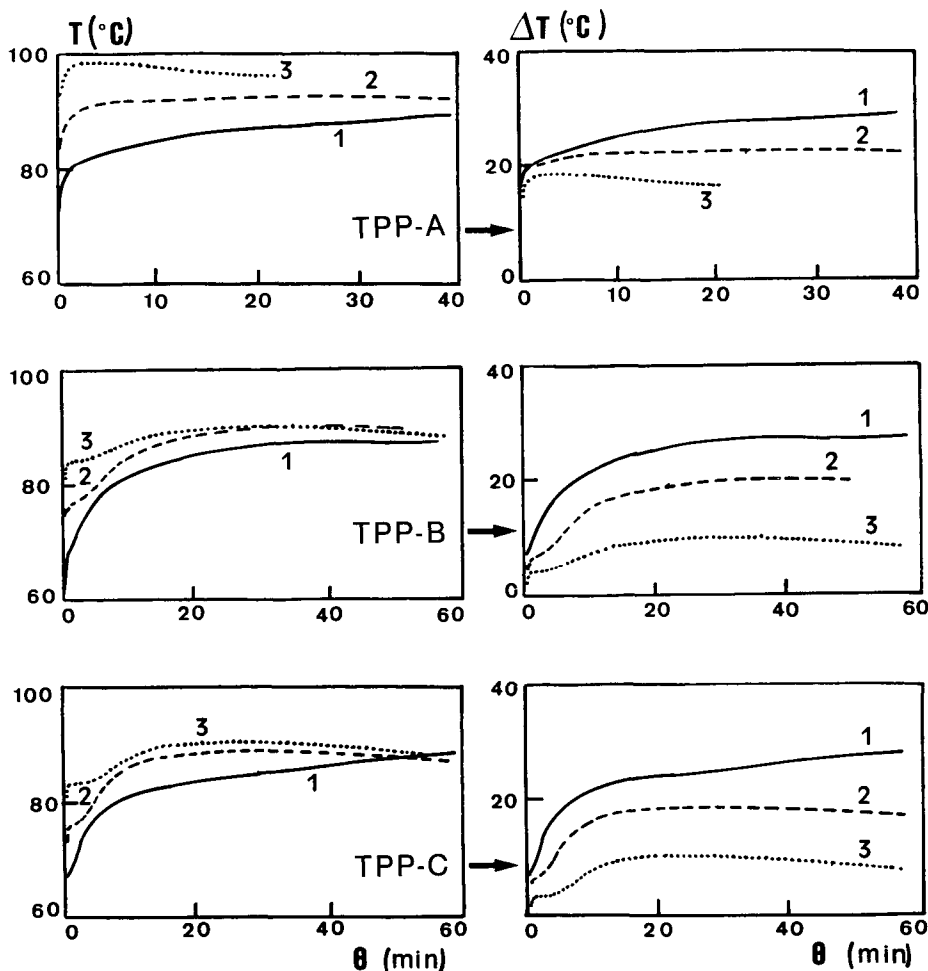


FIG. 1. Influence of temperature and the phase I/phase II ratio on pentasodium triphosphate (TPP) hydration. Stirring, 650 rpm; water hardness, 0°F; initial temperature (°C), 1, 60; 2, 70; and 3, 80.

deduced that when the content of hexahydrate crystals in the reacting system is increased, the period of induction decreases (this decrease is insignificant for percentages of crystals above approximately 4%); the global rate of TPP hydration increases; and the value of the maximum temperature reached decreases.

Influence of water hardness. The effects of water hardness (0, 10, 20, 30 and 40°F) were studied. The experiments were carried out with the three products at initial temperatures of 60, 70 and 80°C. The experiments show that water hardness does not exert a significant influence on the hydration of TPP. These results can be explained by the contribution of calcium ions to the system, as a consequence of the increase in water hardness, being quantitatively insignificant in comparison with the high ionic charge from the Na_2SO_4 added to the initial solution; and the amount of TPP that can be isolated from the reaction medium after the formation of 1:1 complexes with the additional calcium ions (20,21) being not significant.

Hydration of TPP in a detergent slurry. The influence of the initial temperature on the hydration of TPP-B in a detergent slurry with a standard composition (Table 2) is shown in Figure 6.

These results prove that hydration of TPP in a detergent slurry fundamentally depends on the composition of the aqueous phase. The initial temperature has an influence on TPP hydration similar to that observed with the hydration test (Fig. 1). This can be seen in the variations that its increase causes in the initial temperature gradient, the period of induction and the time needed to reach the maximum temperature, *i.e.*, on the global process of TPP hydration.

It is worth pointing out that the thermal changes produced during the hydration of TPP in a detergent slurry are less remarkable than those observed when the hydration test is used. This is a consequence of the dilution of the product in that reaction medium. This fact proves the advantage of the hydration test for an on-site study of the characteristics of TPP hydration.

DISCUSSION

The literature (6,7,16) shows that TPP hydration in a detergent slurry involves a series of intermediate stages that include the solution and further crystallization of the hexahydrate when the solution is supersaturated. These

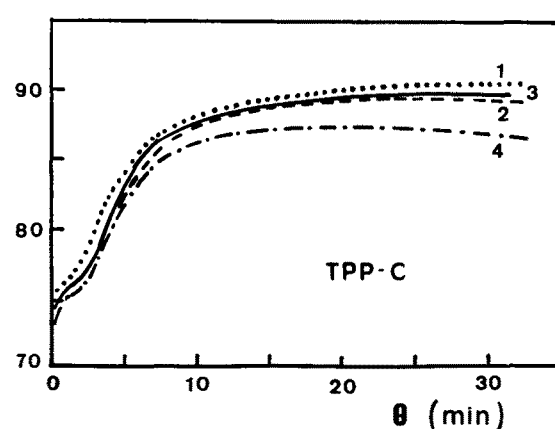
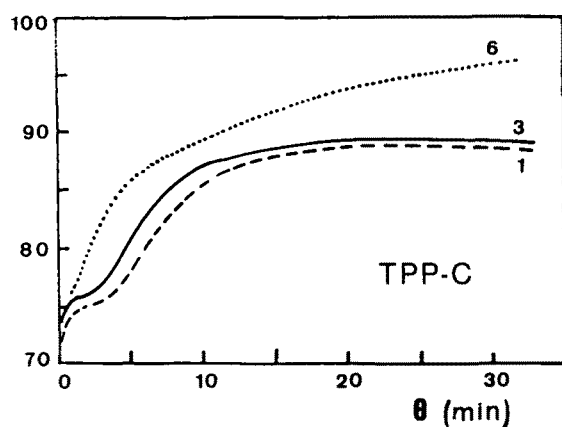
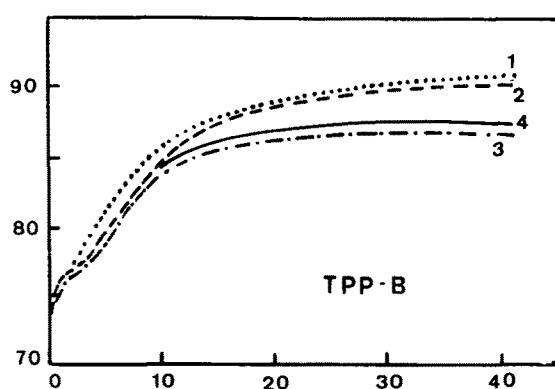
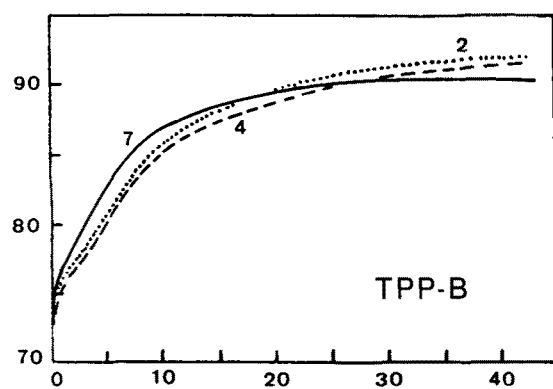
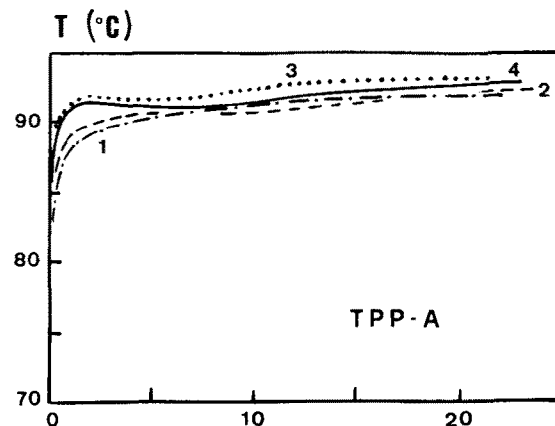
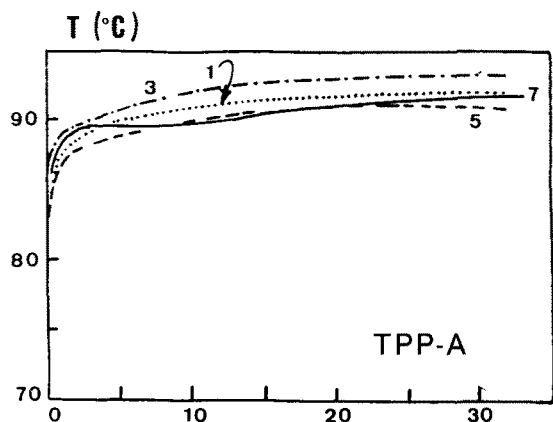


FIG. 2. Influence of particle size on pentasodium triphosphate (TPP) hydration. Stirring, 650 rpm; water hardness, 0°F; initial temperature, 70°C. Size (mm), 1, 0.59–0.125; 2, 0.59–0.063; 3, 0.125–0.053; 4, 0.063–0.04; 5, 0.053–0.04; 6, sifting 0.053; and 7, sifting 0.04.

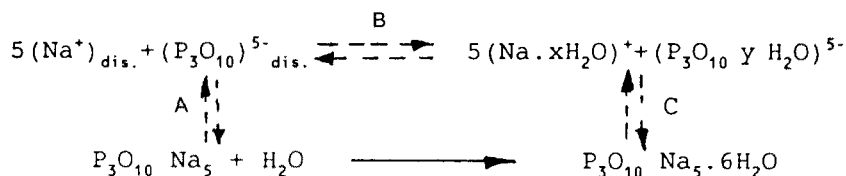
FIG. 3. Influence of stirring on pentasodium triphosphate (TPP) hydration. Water hardness, 0°F; initial temperature, 70°C; stirring (rpm), 1, 450; 2, 850; 3, 1000; and 4, 1400.

stages can be summarized according to the following model:

Stage A represents the solubility equilibrium of anhydrous TPP. This solubility is higher than that of the hexahydrate (3–5), whose formation is represented by equilibrium B.

Equilibrium B implies the formation of solvated ions. When the solution is supersaturated with these ions, precipitation of the hexahydrate takes place, according to equilibrium C.

The process of TPP hydration, considered globally, is



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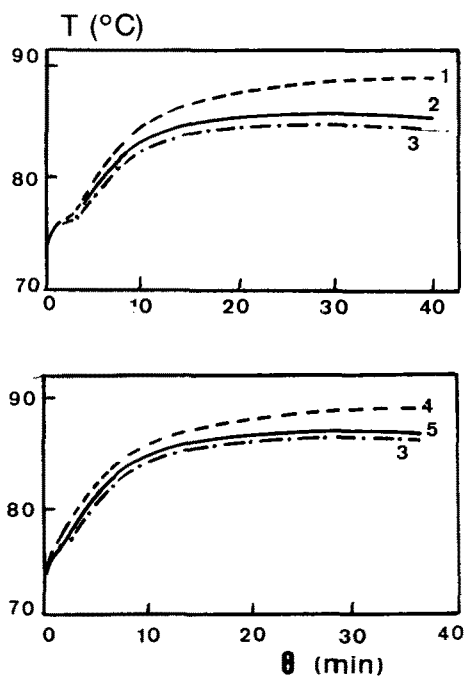


FIG. 4. Influence of stirring on pentasodium triphosphate (TPP)-B hydration. Water hardness, 0°F; initial temperature, 70°C; stirring (rpm), 1, 450-650; 2, 1000; 3, 1400; 4, 450-1000; and 5, 1200. A, size 0.59-0.063 mm; and B, sifting 0.040 mm.

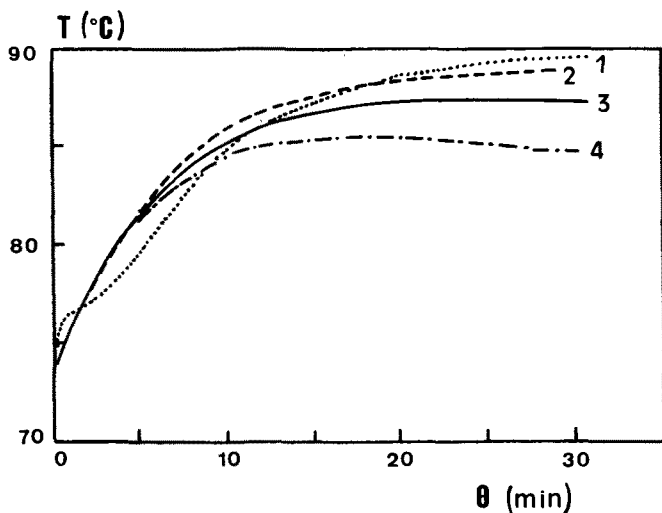


FIG. 5. Influence of the addition of hexahydrate crystals on the hydration of pentasodium triphosphate (TPP)-B. Stirring, 650 rpm; water hardness, 0°F; initial temperature, 70°C. Percentages of crystals of hexahydrate on the total weight (%), 1, 0; 2, 4; 3, 8; and 4, 10 and 15.

irreversible at moderate temperatures. The exact temperature of the transition between the anhydrous and hydrated salt is not known. However, there is experimental evidence to state that the hexahydrate cannot be dehydrated without hydrolytic degradation at temperatures lower than 100-110°C (19,22).

The experimental results can be interpreted from the proposed reaction model, and the influence of the variables studied on each of its stages also can be analyzed.

TABLE 2

Standard Composition of the Detergent

Sodium dodecylbenzene sulfonate	6%
Hydrotrope	1%
Fatty acid + NaOH	3%
Polyoxyethylene (EO = 7) fatty alcohols	3%
Sodium silicate	5%
Na ₂ SO ₄	51%
Sodium carboxymethylcellulose	1%
Builder	30%

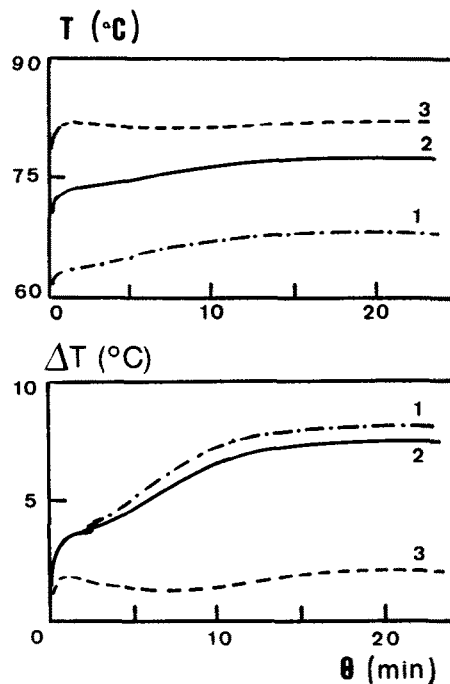


FIG. 6. Influence of initial temperature on hydration of pentasodium triphosphate-B in a detergent slurry. Stirring, 650 rpm; water hardness, 0°F; initial temperature (°C), 1, 60; 2, 70; and 3, 80.

The influence of temperature can affect the three stages of the reaction model proposed. Because the effect of temperature on TPP hydration basically depends on the phase I/phase II ratio, it seems convenient to center the discussion of the results on this fact. The initial gradient of temperature is higher in TPP-A. This is a logical consequence of the greater solubility in water of phase I (3-5), which, by comparison with other compounds, has been attributed to the coordination of the sodium ions in the TPP molecule (23). This is deduced from the experimental results obtained when applying Equation 1 in the initial interval between 0 and 1 min, supposing that the heat losses are insignificant when compared to the heat generated, as can be observed in Figure 7.

From Figure 7 it can be deduced that the TPP transformed into hexahydrate is greater than the content of phase I in the products studied. This indicates that during the initial stage of TPP hydration, solution of both phases takes place, although primarily of phase I. That

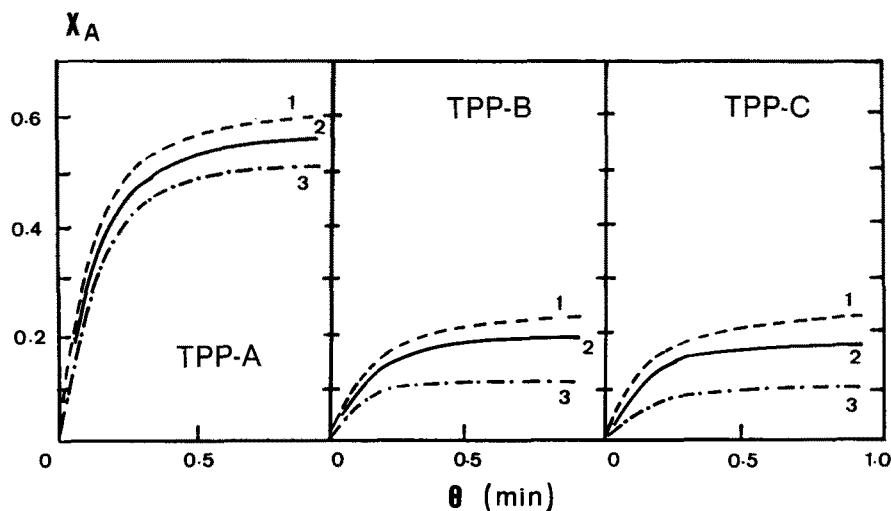


FIG. 7. Influence of initial temperature on the conversion of pentasodium triphosphate (TPP) during the first minute of reaction. Stirring, 650 rpm; water hardness, 0°F; initial temperature (°C), 1, 60; 2, 70; and 3, 80.

is, the conversions at any temperature are greater in the product with a higher content of phase I (TPP-A). From another point of view, the fact that the conversion decreases with increasing temperature contradicts what could be expected of the influence of temperature on TPP solubility (3-5). The unfavorable influence of temperature is more evident in products with a higher content of phase II (TPP-B and TPP-C).

An increase in temperature is unfavorable for the solvation of ions in dissolution (Fig. 7). The decrease in TPP conversion cannot be explained if TPP hydration is controlled by an irreversible chemical reaction (19,22,24). Moreover, the kinetics of this stage are not improved with increasing temperature, as can be deduced from the lower reaction rate ($dX_A/d\theta$) in the interval considered. Therefore, it can be supposed that crystallization of the hexahydrate must have a significant effect on the global kinetics of TPP hydration, if the proposed model is acceptable.

The period of induction observed (Fig. 1) in the products with a higher content of phase II (TPP-B and TPP-C) is congruent with a process of nucleation. An increase in temperature exerts an unfavorable influence on the number of nuclei formed and on the rate of nucleation (25), as can be deduced from Figure 1. The lack of an induction period in the hydration of TPP-A may be due to a "catalytic" effect exerted by higher content of phase I. This could produce regions of high supersaturation in which the hexahydrate crystallizes (16). In the stage in which crystallization of the hexahydrate takes place, the formation of nuclei and, consequently, the global process of hydration of TPP may be favored if small nuclei are initially added to the product used (TPP-C). This can be deduced from the literature (6,7) and is supported by the experimental results represented in Figure 5. The reduction of the induction period with the addition of hexahydrate crystals supports the importance of hexahydrate crystallization in TPP hydration.

The experimental results obtained with TPP-A and TPP-B do not indicate a definite tendency in the influence of

particle size on hydration of the product. This influence should be more evident in products with a higher content of phase II because their solubility and rate of dissolution are lower (7). It can be concluded that TPP dissolution does not have a significant influence on the global process of TPP hydration. The results obtained with the TPP-C product fit a model in which hexahydrate crystallization is the stage that controls the global process. In other words, if particle size is reduced, the number of hexahydrate crystals in the TPP-C product increases, which must facilitate hexahydrate crystallization during the initial stages of the process.

The unequal influence of stirring rate on the initial period confirms the hypothesis that anhydrous salt dissolution does not have a significant influence on TPP hydration kinetics. The influence of the stirring rate (over the range studied) on the kinetics of the process, especially with TPP-B and TPP-C (Fig. 3), leads to the conclusion that TPP hydration may depend on the nucleation and growth of crystals. The growth rate of the hexahydrate crystals consists of two resistances (26). These resistances are a function (25) of the stirring rate and of the system (especially phase I/phase II ratio). This agrees with the results shown in Figure 3 and 4. The results show that the reaction model is acceptable for the behavior of TPP hydration in a detergent slurry. In fact, this can be inferred from the influence of each of the variables on TPP hydration.

The negative or insignificant influence of initial temperature, of stirring rate and of particle size in the initial stages of TPP hydration indicate that the dissolution of the anhydrous salt does not have a significant effect on the global process. The unfavorable influence of temperature on the degree of conversion reached and on its kinetics seems to indicate that the formation of solvated ions does not offer a significant resistance in TPP hydration.

The crystallization of the hexahydrate seems to be the stage that controls the process. The equilibrium and the kinetics corresponding to this stage are affected by two

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resistances: (i) resistance to nucleation, evident in TPP with a higher content of phase II. This is deduced from the unfavorable influence of temperature on the induction period and from the reduction of that period when crystals of hexahydrate are added to the system; and (ii) resistance to the growth of the hexahydrate crystals formed. This is deduced from an unfavorable influence of a temperature increase and the influence of stirring during the process of hydration of TPP.

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REFERENCES

- Hollingsworth, M.W., *J. Am. Oil Chem. Soc.* 55:49 (1978).
- Nagarajan, M.K., and H.L. Paine, *Ibid.* 61:1475 (1984).
- Van Wazer, J.R., *Phosphorus and Its Compounds*, Vol. I, Interscience, New York, 1958, p. 414.
- Hurst, T.L., *Ibid.*, Vol. II, edited by Van Wazer, J.R., Interscience, New York, 1958, p. 1213.
- Harris, J.C., and J.R. Van Wazer, *Ibid.*, Vol. II edited by Van Wazer, J.R., Interscience, New York, 1958, p. 1732.
- Shen, C.Y., and J.S. Metcalf, *Ind. Eng. Chem. Product Res. Dev.* 4:107 (1965).
- Nielen, H.D., and H. Landgraber, *Tenside Deterg.* 14:205 (1977).
- Landgraber, H., *Seifen-Ole Fette Wachse* 109, 318 (1983).
- Grobe, J., and H.D. Nielen, *Tenside Deterg.* 20:285 (1983).
- Guerrero Conejo, A., J.M. Rodríguez Patino, C. Gallegos Montes, L. Albea Carlini and V. Flores Luque, *Jorn. Com. Esp. Deterg.* 17:77 (1986).
- Guerrero Conejo, A., J.M. Rodríguez Patino, L. Albea Carlini, C. Gallegos Montes and V. Flores Luque, *J. Am. Oil Chem. Soc.* 66:261 (1989).
- Guerrero Conejo, A., J.M. Rodríguez Patino, C. Gallegos Montes and V. Flores Luque, *Chem. and Biochem. Eng. Q.* 5:125 (1991).
- Rodríguez Patino, J.M., A.F. Guerrero Conejo, C. Gallegos Montes and V. Flores Luque, *Proceedings of the 1st International Congress on Solid and Liquid Wastes: Their Best Destination*, Tenerife, Spain, 1990, p. 95.
- Guerrero Conejo, A., J.M. Rodríguez Patino, C. Gallegos Montes and V. Flores Luque, *Jorn. Com. Esp. Deterg.* 19:387 (1988).
- Guerrero Conejo, A., J.M. Rodríguez Patino, C. Gallegos Montes and V. Flores Luque, *Ibid.* 20:271 (1989).
- McGilbery, J.D., *ASTM Bull.* 45: (1953).
- Henning, K., and H. Schonborn, *Tenside Deterg.* 13:70 (1976).
- Sorbe, G., *Jorn. Com. Esp. Detergent.* 15:245 (1984).
- Quimby, O.T., *J. Phys. Chem.* 56:603 (1954).
- Bousi, F., *Riv. Ital. Sost. Grasse* 57:248 (1980).
- Chang, D.M., *J. Am. Oil Chem. Soc.* 60:618 (1983).
- Hafford, B.C., *Ind. Eng. Chem.* 46:1938 (1954).
- Tob, A.D.F., *The Chemistry of Phosphorus*, Vol. III, edited by A.F. Trotman-Dickinson, Pergamon Press, London, 1973.
- Shen, C.H., J.S. Metcalf and E.V. O'Grady, *Ind. Eng. Chem.* 51:717 (1959).
- Garside, J., *Chem. Eng. Sci.* 40:3 (1985).
- McCabe, W.L., and J.C. Smith, *Unit Operations of Chemical Engineering*, Ed. Reverté, Barcelona, 1975.

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