

Rheokinetic Analysis of the Hydration of Pentasodium Triphosphate in a Detergent Slurry

J.M. Rodríguez Patino*, A. Guerrero and C. Gallegos

Departamento de Ingeniería Química, Facultad de Química, Universidad de Sevilla, 41012 Sevilla, Spain

The main objective of this research was to analyze, from a rheokinetic point of view, the hydration of pentasodium triphosphate (TPP) in a detergent slurry with a standard composition. A torque rheometer (Brabender Plastograph) with a roller-type measuring system was used. The influence of temperature, TPP quality, system agitation and concentration of dry substances on the total torque of the samples has been studied. From the experimental results it can be concluded that all of these parameters, as well as the reaction time, influence the consistency of the samples. The kinetics of the process are controlled by diffusional resistances.

KEY WORDS: Builder, detergent, pentasodium, pentasodium triphosphate hydration, rheokinetic, suspension rheology, torque rheometry.

The majority of industrial processes for manufacturing laundry detergent powders are based on the use of pentasodium triphosphate (TPP), either as the only builder in the formulation or as part of a builder mixture (1–3), which is the norm in most industrialized countries (4–6). These countries are limiting the use of TPP because of ecological problems related to the eutrophication of lakes and other bodies of water (7) and are embracing legal or volunteer programs to restrict or even forbid its presence in detergents (8).

From a strictly industrial point of view, the use of TPP in detergents presents some technical problems in the plants where their slurries are processed, because of the hydration of TPP in the bulk suspension. This hydration, which has been extensively studied (9–12), 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 production efficiency and detergent properties. Hence, the slurry, before being injected into the spray-drying tower, must have specific properties within narrow limits (9–14).

Taking these problems into account, it is necessary to verify that phosphorus is present in the final products as hexahydrated pentasodium triphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}\cdot 6\text{H}_2\text{O}$). This means monitoring the hydration process while studying the influence of its substitution for other builders in that process.

In a previous paper (15), we analyzed the influence that different technical parameters exert on the hydration of the TPP in a slurry containing an aqueous solution of Na_2SO_4 . It was concluded that the hydration occurs through a series of intermediate steps, comprising dissolution of the anhydrous salt, hydration of ions in solution and, finally, crystallization of hexahydrate (15).

The main objective of this paper is to analyze, from a rheokinetic point of view, the hydration of TPP in a detergent slurry with a standard composition. This study also provides basic knowledge of the intermediate products for their correct handling during the industrial process and the

basis for studying the influence that partial or total substitution of TPP exerts on the process.

EXPERIMENTAL PROCEDURES

Equipment and methods. The hydration reaction of TPP has been recorded by plotting torque values ($M-M_0$) against time of reaction (θ), where M is the total measured torque of the slurry during the hydration of TPP and M_0 is the measured torque before the addition of TPP. The reaction bulk is a detergent slurry with a standard composition. The process is complete when the torque reaches a maximum value after a certain reaction time (9–12). This value is referred to as the characteristic torque (M^*). This method is of great interest because the data obtained on the change of the slurry consistency are important for the in-plant handling of the product (16).

The experimental results were obtained with a Brabender Plastograph (PL 3S model), which can be used in continuous processing operations and which provides the agitation necessary to obtain a well-integrated mixture of the slurry components. The apparatus is fitted with a roller-type measuring system with two sigmoid, counter-rotating blades turning with different angular velocities (ratio, 3:2). A detailed description of this instrument and its operational conditions may be found in the literature (17,18). The temperature is controlled by circulating water through a thermostat, accurate to $\pm 0.1^\circ\text{C}$, and a thermocouple in direct contact with a constant value during the hydration.

Test variables. Because the rheokinetics of TPP hydration depends on several factors, the following variables have been used: (i) Quality of TPP—three commercial products containing 94–96% TPP on a dry basis (56.5% P_2O_5) with different proportions of phase I and phase II TPP (19) were used: TPP-A (25% phase I); TPP-B (12% phase I); and TPP-C (1% phase I, partially hydrated). A detailed description of the products is included in a previous article (15). (ii) Concentration of slurry—a detergent formulation of standard composition was prepared by adding the following components to water in this order: sodium dodecylbenzene sulfonate, 6%; hydrotrope (sodium toluene sulfonate), 1%; fatty acid with a mol wt of 270.87 (mixture of palmitic and stearic acids) neutralized by sodium hydroxide, 3%; polyoxyethylene (EO 7) fatty alcohol ($\text{C}_{13}\text{--}\text{C}_{15}$), 3%; sodium silicate, 5%; anhydrous sodium sulfate, 51%; sodium carboxymethylcellulose, 1%; and TPP, 30%. The slurry concentrations studied (W) were 65, 70, 75 and 80% w/w. (iii) Temperature of the sample (T)—measurements were carried out isothermally at 60, 70 and 80°C . (iv) Slurry agitation (Ω). The slurry was subjected to different degrees of agitation, corresponding to the following rotor angular velocities: 60, 100, 140 and 180 rpm.

RESULTS

The influence of temperature on TPP hydration, which can be deduced from the experimental results presented in

*To whom all correspondence should be addressed at Dept. de Ingeniería Química, Facultad de Química, Universidad de Sevilla, c/Prof. Gascía González, s/n. 41012 Sevilla, Spain.

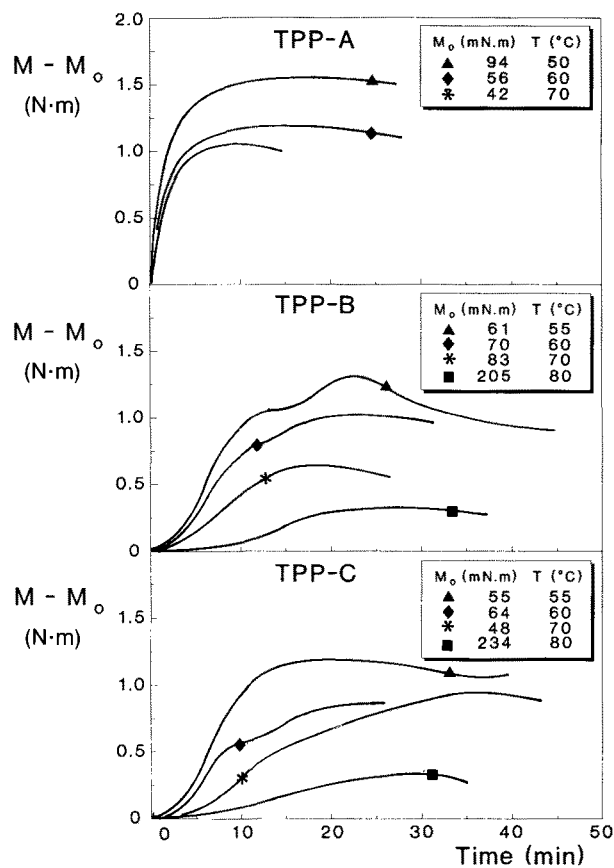


FIG. 1. Influence of temperature on the hydration of pentasodium triphosphate (TPP). Angular velocity, 100 rpm; concentration of dry substances, 75%.

Figure 1, depends on the phase I/phase II ratio in the product. For products with higher phase I content (TPP-A), the overall hydration velocity increases with temperature, thereby decreasing the torque of the system. The variation of torque with time, and consequently the hydration velocity, is characterized by the presence of an induction time in products with the highest content of phase II (TPP-B and TPP-C). Thus, a rise in temperature produces an increase in the induction time, but overall hydration velocity and torque decrease when using these products. Once the induction time is over, the overall hydration velocity is not significantly influenced by temperature. An increase in the phase I/phase II ratio has positive effects on the hydration of TPP, improving the kinetics of the process independently of the process temperature. Nevertheless, the consistency of the system rises when using products with a higher phase I content.

Experimental results referring to the influence of the system agitation on the hydration of TPP are presented in Figure 2. An increase in agitation produces both higher values for the initial and overall hydration velocities and for the system torque in products with the highest content of phase I (TPP-A). For systems with the highest content in phase II (TPP-B and TPP-C), an increase in agitation produces both higher values for the overall hydration velocity and torque of the system. Nevertheless, significant influence of agitation on the induction time is not observed. The influence of agitation on the hydration of

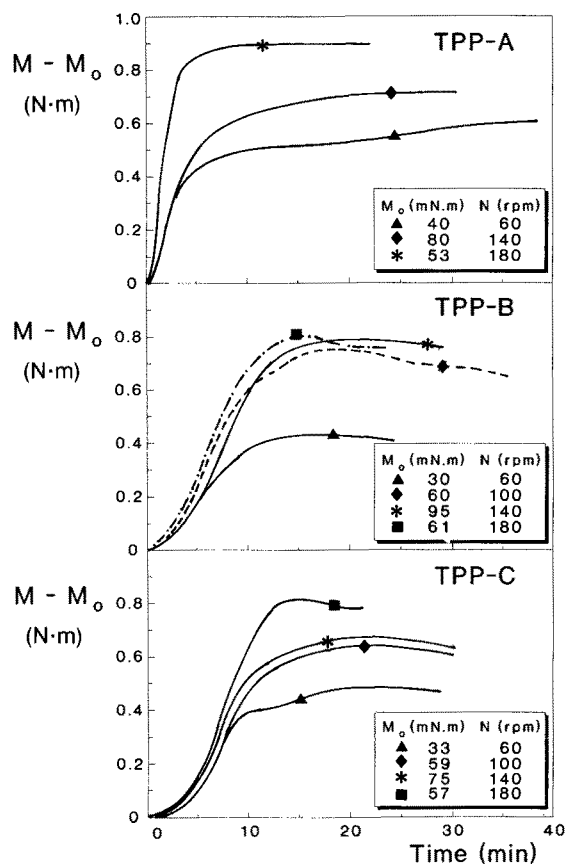


FIG. 2. Influence of stirring on the hydration of pentasodium triphosphate (TPP). Temperature, 60°C; concentration of dry substances, 70%.

TPP is more important in products with maximum content in phase I because of their higher consistency.

The influence of the concentration of dry substances on the hydration of TPP can be observed in Figure 3. An increase in concentration generally produces a reduction of the overall hydration velocity of the product and an increase in the torque. This effect is not significant for products containing TPP-A, which may be attributed to the higher hydration velocity they present. Moreover, a rise in the induction time with increasing dry-substance concentration can be observed in products with the highest phase II content. These effects are more important at the highest concentration of dry substances (80% w/w). Thus, the values of the parameter $M^* - M_0$ increase 209, 221 and 278% for TPP-A, TPP-B and TPP-C type products, respectively, when dry-substance concentration is changed from 75 to 80%. Whatever this concentration is, the consistency of the system is higher in products with greater phase I content. Moreover, the increase in the initial consistency of the system after the addition of TPP of the TPP-A type product is especially noteworthy.

DISCUSSION

Due to the fact that all the variables influence both the system kinetics and consistency, they must be analyzed separately.

From a kinetic point of view, the hydration of TPP in

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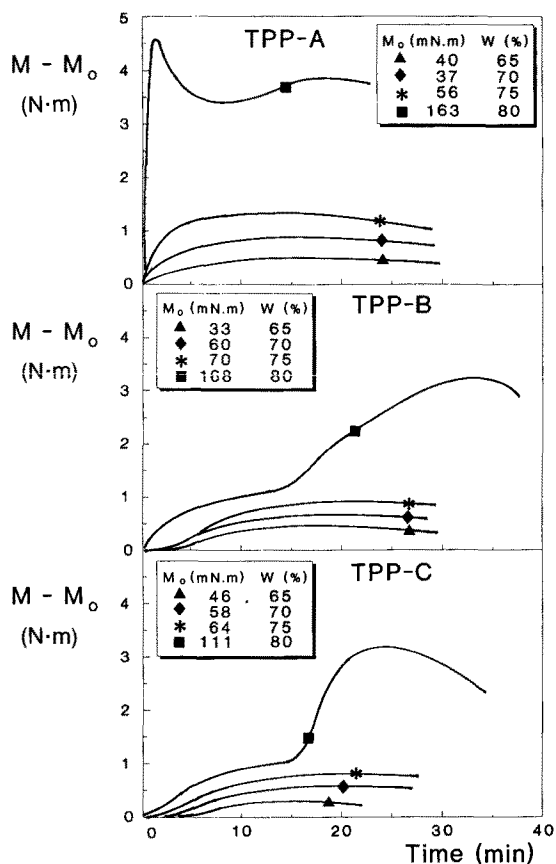


FIG. 3. Influence of the concentration of dry-substance on the hydration of TPP. Temperature, 60°C; angular velocity, 100 rpm. Abbreviations as in Figure 1.

a detergent slurry may be influenced by diffusional (TPP dissolution and crystallization of the hexahydrate) and chemical steps (solvation of ions in solution). Their relative importance can be deduced from the analysis of experimental results.

The influence of the resistance of the chemical step on the overall kinetics of the process is not significant, as can be deduced from the influence of temperature or dry-substance concentration on the overall hydration velocity of the TPP. In general, both variables have a positive influence on the chemical kinetics, the effect of temperature being exponential and upon the reaction order, especially the concentration of dry substances.

Consequently, the hydration of the TPP is controlled by diffusional resistances. This means that: (i) The induction time observed in products with a high phase II content is characteristic of a nucleation process. A rise in temperature has a negative influence, above a threshold value, on this process (20). The fact that there is no significant influence of temperature on the overall hydration velocity of the TPP after the induction time may be due to effects in contrary directions—a rise in temperature decreases both the consistency of the system and the diffusional resistances; on the other hand, both the nucleation process and crystal growth velocities are decreased. (ii) The absence of an induction time in products with a higher phase I content may be due to the presence of

regions with high supersaturation, favoring nucleation of the hexahydrate because of the faster rate of dissolution of phase I (19). The fact that the overall hydration velocity of TPP increased with agitation, without significantly effecting the initial steps of the process, may be due to a higher quantitative influence of the hexahydrate crystallization than the dissolution of the TPP. (iii) The increase in overall hydration velocity of TPP with agitation may be due to a reduction of the diffusional resistances, which favor TPP dissolution and the diffusion of solvated ions and nuclei to the hexahydrate crystals surface, thereby facilitating their growth. This is important for systems of high consistency, like the ones studied in this research.

The results obtained by increasing the dry-substance content of the slurry support the previous conclusions (Fig. 3). The high consistency of the system that contains 80% dry substances does not permit the diffusion of the ions in solution, which has a negative influence on the process kinetics, particularly for the TPP-A product.

From a rheological point of view, the consistency of the system during TPP hydration depends on several different factors—temperature and its variation during the hydration, angular velocity of the mixer, concentration of dry substances and reaction time.

The increase in consistency during the process is thought to be due to a decrease in water content as a result of TPP hydration. In relation to products with the highest content of phase I, the faster hydration velocity, during the initial steps and in the total process, yields higher torque values. Moreover, different authors hold that the hexahydrate crystals are more tightly packed and smaller in these products (7). This could explain the high initial consistency of the system after the addition of TPP-A to the slurry (Fig. 3a). All these problems could influence the handling of products with high content of phase I during industrial processing, because of the appearance of clusters in the slurry that would impede its flow and, eventually, its processing in the spray-drying tower.

The decrease of slurry consistency, after the characteristic torque is reached, may be due to a double effect: (i) If the growth of the hexahydrate crystals is not complete at the time of the appearance of the torque overshoot, this would yield a lower significance of the shear in the system, related to a decrease in specific area of the particles. (ii) Secondly, the torque overshoot could be related to the appearance of structural breakdown caused by shear forces. This behavior may be only partially reversible and is commonly found in concentrated suspensions (21,22). The breakdown of the system structure after the hexahydrate crystallization yields a much more stable configuration of the particle in the suspension, with minimum flow resistance.

The amount of torque overshoot may be quantitated by means of an equation similar to the one previously proposed by Ganani and Powell (21):

$$S = (M^* - M_s)/M_s \quad [1]$$

where M_s is the torque corresponding to a shear time when the steady-state has been reached.

The amount of torque overshoot *vs.* temperature and dry-substance content can be observed in Figure 4. "S" increases with the dry-substance concentration in the

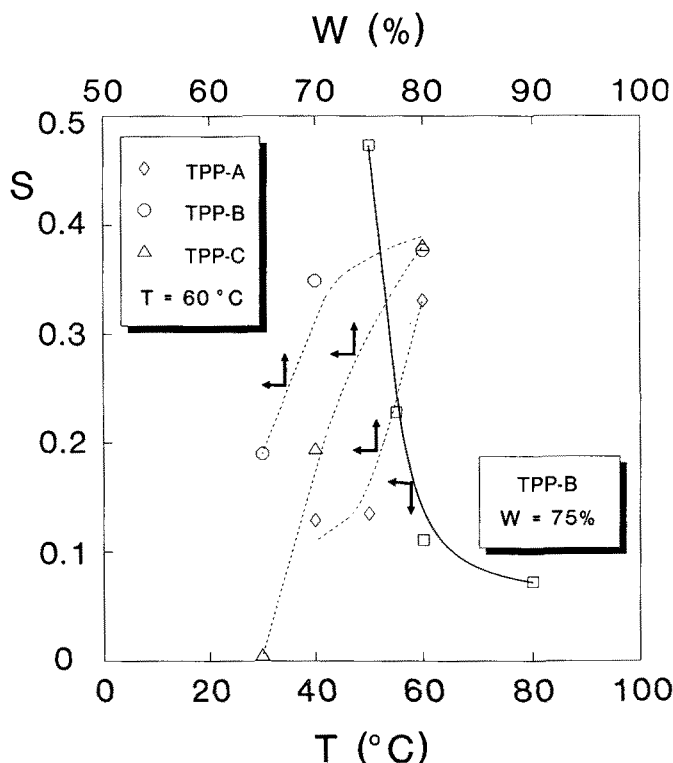


FIG. 4. Torque overshoot vs. temperature and dry-substance content.

slurry, or when temperature decreases; in other words, when the solid characteristics of the slurry are more prevalent. If the amount of torque overshoot is related to the structural breakdown of the slurry, the results can be explained according to the influence of shear on the structure, which clearly increases with the solid content of the slurry. These results are similar to those obtained with other structured systems (22,23). Finally, the TPP quality does not exert a significant influence on the amount of torque overshoot, as can be deduced from Figure 4.

The irregular geometry of the sensor systems used by torque-rheometers creates a complex shearing motion in the slurry. In addition to this, the existence of time-dependent phenomena makes it impossible to obtain absolute rheological variables from torque or angular velocity values, contrary to results previously published by the authors when steady-state tests were carried out (12). That is why the consistency of the system is quantitated by the torque values. The characteristic value of M^* can be considered as an important parameter of the process from a technical point of view, and has been used to discuss, from a rheological point of view, the influence that different variables exert on the consistency of a detergent slurry in the course of TPP hydration.

The influence of temperature on the characteristic torque of the system can be observed in Figure 5. The values of M^* for TPP-A are lower for low temperatures, due to the impossibility of dissipating the heat produced during its hydration. This is not the case for the hydration of products with a high content of phase II, because it is carried out without change in temperature. The decrease of slurry consistency with a rise in temperature is a well

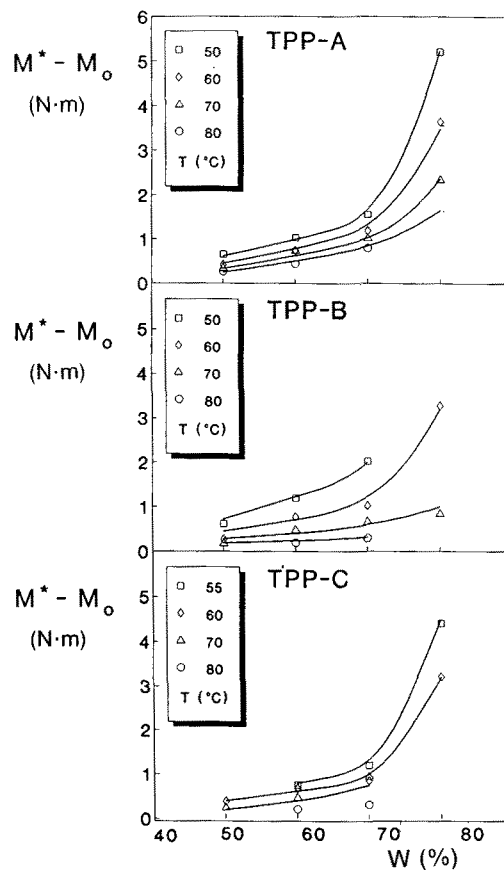


FIG. 5. Influence of temperature on the characteristic torque of the slurry. Angular velocity, 100 rpm.

known phenomenon in suspensions (24–27). This dependence may be due to a double effect—viscosity of the liquid phase decreases with increasing temperature (26) and the flocculation level of the particles in the suspension changes (24). In these products, the characteristic torque variation with temperature has been quantitated by an equation similar to the Arrhenius plot, yielding:

$$M^* - M_0 = A e^{B/T} \quad [2]$$

where A and B are parameters that depend both on the dry substances and quality of TPP. T is the temperature in degrees Kelvin. Values of parameters A and B are given in Table 1, as well as the linear regression coefficient, r .

An increase in the angular velocity of rollers produces higher characteristic torque values, as a consequence of a stronger shear (Fig. 6). The relationship between both variables is influenced by the shear time because of the structural breakdown behavior of these systems, as can be deduced from the results in experiences up to steady shear (Fig. 4). If the variation of the characteristic torque of the system with the angular velocity of the rollers (Fig. 6) could be related as in steady-state shear (12), the plastic-like rheological behavior of the slurry would be similar to that shown by other concentrated suspensions (28,29). This supports the interrelationship between the change in consistency with angular velocity of the roller and the structural breakdown due to shear forces (30,31).

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TABLE 1

Parameter Values of Equation 2						
W (%)	TPP-A	r	TPP-B	r	TPP-C	r
65	A	0.0221	$1.2 \cdot 10^{-4}$			
	B	3307	5043	0.966		
70	A	0.2822	$2.6 \cdot 10^{-6}$		$3.6 \cdot 10^{-5}$	
	B	2633	6450	0.976	5548	0.975
75	A	1.1282	$1.3 \cdot 10^{-6}$		$8.7 \cdot 10^{-6}$	
	B	2321	6460	0.992	5548	0.999
80	A	0.0067				
	B	4382		0.997		

^aW, w/w % of the slurry concentrations studied; TPP, pentasodium triphosphate; r, linear regression coefficient.

TABLE 2

Parameter Values of Equation 3 ^a						
T (°C)	TPP-A	r	TPP-B	r	TPP-C	r
50	C	59.36	41.47			
	D	0.133	1.120	0.962	0.997	
55	C	108.6	120.9		134.5	
	D	0.168	0.170	0.971	0.968	0.966
60	C	49.67	24.60		34.12	
	D	0.139	0.113	0.979	0.940	0.946
70	C	24.49	4.013			
	D	0.121	0.074	0.988	0.980	
80	C	12.68	1.14			
	D	0.111	0.055	0.999	0.950	

^aAbbreviations as in Table 1. T, temperature.

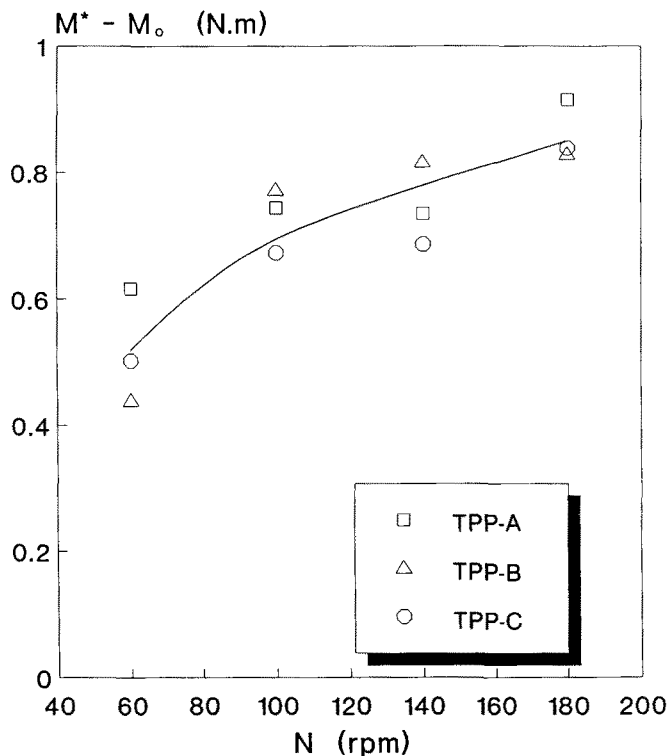


FIG. 6. Influence of the angular velocity on the characteristic torque of the slurry. Temperature, 60°C; concentration of dry substances, 70%.

The effect produced by the dry-substance concentration on the characteristic torque is similar to that previously reported by other authors on the interdependence of the relative viscosity of the suspension and the volume fraction of solids (32-35). Figure 5 shows that the value of M^* increases with dry-substance concentration. This influence is much more dramatic when the dry-substance concentration is nearly 80%. The influence of the dry-substance concentration on the characteristic torque is more important as temperature decreases. This may be due to the fact that the continuous phase is supersat-

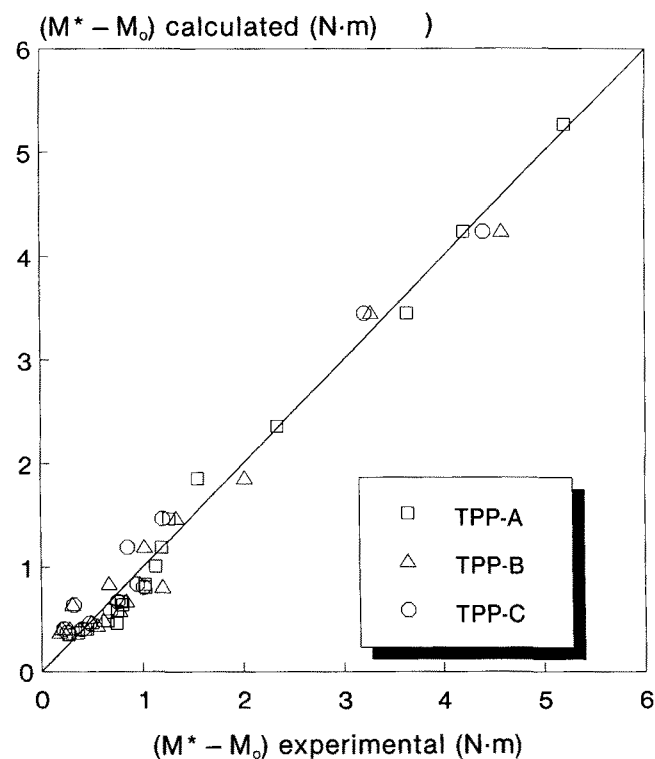


FIG. 7. Experimental vs. calculated characteristic torque of the slurry. Angular velocity, 100 rpm; temperature, T(°C), 50 < T < 80; concentration of dry substances, W(%), 65 < W < 80. Abbreviations as in Table 1.

urated in some of the slurry components, especially in $\text{Na}_5\text{P}_3\text{O}_{16} \cdot 6\text{H}_2\text{O}$ and Na_2SO_4 , which crystallize as temperature decreases, producing an increase of solid concentration in the suspension. The increase of the characteristic torque with the dry-substance content, observed in Figure 5, is a well known fact in the rheology of suspensions (32,33). In fact, it is possible to propose an equation relating both variables for all TPP qualities, similar to

those of Sikdar and Ore (33,34) and Krieger and Dougherty (35):

$$M^* - M_0 = C e^{D(W-100)} \quad [3]$$

where C and D are parameters that depend on temperature and TPP quality. Their values are shown in Table 2, as well as the linear regression coefficient, r.

The interrelationship between the influence that temperature and dry-substance concentration exert on the characteristic torque of the system, as can be deduced from the experimental results, yields an empirical equation that includes the effect that both variables exert on the detergent slurry, without influence of the phase I/phase II ratio in the TPP. This equation, similar to others previously published relating influences of temperature and dry substances on relative viscosity of suspensions (36-38), can be expressed as:

$$M^* - M_0 = 334.7 + 54.5 \cdot 10^4 e^{(W-100)/(247/T-1)} \quad [4]$$

Experimental and calculated characteristic torque values are compared in Figure 7. The linear regression coefficient for Equation 4 is $r = 0.989$.

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