

Effect of processing parameters on the particle size and stabilisation of titania sols

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A systematic analysis of the main parameters affecting the characteristics of titania sols for photocatalytic applications prepared from the hydrolysis of titanium i-propoxide (TIP) is presented. Stable monomodal sols were obtained at peptization temperatures between 50°C and 70°C, for water/alkoxide molar ratios ranging from 250 to 1000 and acid/alkoxide molar ratios ranging from 0.4 to 0.7. Unstable sols with bimodal distributions were obtained at higher peptization temperatures. The peptization temperature was the parameter with the greatest influence, followed by acid concentration, whereas the water/alkoxide ratio showed little influence. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) were used to verify the primary particle size as measured by photon correlation spectroscopy (PCS). The observations are explained using the Derjaguin, Landau, Verwey and Overbeek (DLVO) theory on suspension stability.

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1. Introduction

New applications involving titanium dioxide are emerging [1], and many of them involve sol gel processing. Of particular interest is the production of photoactive titania coatings produced by dip coating for a number of novel applications including sterilization [2, 3] and self cleaning materials [4]. Despite the increasing interest in this field, only a few reports in the literature have studied the dependence of the particle size of the coating (and therefore the particle size of the sol) with the performance of the coating [5]. In order to establish this correlation in a systematic way, a stable and well-characterised sol must first be obtained. In the literature there is no consensus for the optimum methodology for the preparation of titania sols. This is confirmed also by a lack of existence of any standard on the subject by any of the recognised standards organisations such as BS, ISO, ASTM, etc. Research groups have developed their own preparation routes, each giving rise to sols with different properties, mainly particle size, concentration and stability, which are important parameters for a subsequent coating.

It has been shown, although not necessarily related to coating applications, that it is possible to obtain sols with different particle size by changing certain parameters of the hydrolysis-peptization process [5–11]. For example, by increasing the water/alkoxide ratio, the particle size of the titanium oxide can be reduced

[5, 6]. It has also been shown that higher values of water/alkoxide ratio (>30) lead to lower concentrations of OR and OH groups in the poly-condensed material from titanium alkoxides [7] and the ratio $\text{TiO}_2/\text{Ti}(\text{OR})_4$ can be increased up to 96 wt%, after drying at 120°C and calcining at 500°C, thus making a more efficient reaction. The same paper showed that for the conditions tested, an acid/alkoxide ratio between 0.15 and 0.30 led to the most stable sol (based on there being no precipitate after 200 days). Another study has shown that alcohol type and concentration are parameters that can influence the particle size of the final sol [8]. Look and Zukoski [9] and Barringer and Bowen [10] recognised the importance of electrolytes in the stability of the sol, and carried out electrophoretic mobility measurements as a function of HCl concentration, and of electrolytes such as KCl, respectively. Vorkapic and Matsoukas carried out a more systematic study using a concentration of 220 mol. water/mol. alkoxides [11]. From this work important conclusions obtained were: (a) a more stable sol was obtained using acid concentrations of 0.5 mol. $\text{HNO}_3/\text{mol. Ti}$; (b) peptization temperature was an important factor in determining the final particle size of the sol; and (c) the addition of alcohol to the hydrolysis had a detrimental effect on the peptization, yielding larger particles.

So far, no systematic study has been done showing the combined effect of temperature, acidity and water/alkoxide ratio on the stability and particle size

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of the sol, investigating how combinations of these factors affect the final properties of the sols. This paper presents research carried out to define, quantify and analyse these combined effects and propose a methodology for the production of titania sols of predefined particle size.

2. Definition of variables

The variables used in this paper are peptization temperature, T , water/alkoxide molar ratio, WA, and nitric acid/alkoxide molar ratio, NA, where WA and NA are defined as follows:

$$WA = \frac{n(\text{H}_2\text{O})}{n(\text{TIP})} \quad (1)$$

$$NA = \frac{n(\text{HNO}_3)}{n(\text{TIP})} \quad (2)$$

where $n(\text{H}_2\text{O})$, $n(\text{TIP})$ and $n(\text{HNO}_3)$ are the moles of water, titanium isopropoxide, TIP, and nitric acid respectively.

3. Experimental procedure

3.1. Design of experiments

The values for the design of experiments were chosen bearing in mind photocatalytic coating applications, i.e. small particle size (large surface area) and taking into account findings from previous studies [5, 6, 8, 11, 12]. They are presented in Table I. Neither steric stabilisation nor stabilisation by other electrolytes were considered, since these may lead to contamination, reducing photocatalytic activity of the coatings (e.g. ions such as Na^+ inhibit the efficiency of titania photocatalysts [13]). It has also been found that it is peptization rather than hydrolysis that determines the properties of the final sol [11]. Therefore the parameters that influence the peptization process rather than the hydrolysis process were investigated.

3.2. Methodology for sol preparation

The reagents used were: HNO_3 (Aldrich reactive grade, specific gravity of 1.42 g/cm^3). TIP (Aldrich reactive grade, >98%) and triply deionised water, TDW, with a minimum resistivity of $18.2 \text{ M}\Omega\text{-cm}$. For all sol preparations 500 g of titania was prepared. Hydrolysis of the alkoxide was performed by injecting the required amount of TIP into acidified TDW that was at the peptization temperature. The mixture was stirred vigorously until peptization was complete, 5–12 h. This was clearly recognised as the de-agglomeration of the white precipitate was accompanied by a colour change of the sol to a characteristic bluish colour.

TABLE I Variables used in the design of experiments

Parameter	Values		
$T(^{\circ}\text{C})$	50 ± 3	70 ± 3	90 ± 3
WA	250 ± 1	500 ± 1	1000 ± 1
NA	0.40 ± 0.01	0.50 ± 0.01	0.66 ± 0.01

3.3. Sol characterisation

Particle size analysis of the sols was carried out on DynaPro-801 TC, scatter angle of 90° , at a temperature of 20°C . All results are the average of at least two independent measurements with 10 readings each. Visual monitoring of sols left in undisturbed bottles for 5 months was carried out to inspect for any precipitate depositing on the bottom. Micrographs for image analysis were obtained with a transmission electron microscope (JEOL 2000FX) at 200 kV. Selected samples were diluted approximately 1:130 with TDW and then mounted on carbon-coated copper grids. Particle size was carried out with image analysis using Scion Image Software [14] by measuring the cross sectional area of a particle and transforming to a sphere of equivalent diameter. The scale bar provided by the microscope was used as the calibration source for the image analyser. For X-ray diffraction, XRD, analysis, ground powder from sols dried at 50°C were analysed on a Siemens D500 diffractometer using a $\text{Cu K}\alpha$ ($\lambda = 0.15405^{\circ} \text{ nm}$) source.

4. Results and discussions

4.1. Effect of temperature, alkoxide concentration and acidity on particle size

4.1.1. Sols prepared with WA = 250

A graph showing the combined effect of NA and T on the percentage mass of the majority particle size, % Mass 1, is shown in Fig. 1 (i.e. % Mass 1 = 100 for a monomodal-sized sol). It can be seen that peptizing at $50\text{--}70^{\circ}\text{C}$ with NA values of 0.4 to 0.6 yielded mostly monomodal sizes.

The corresponding particle sizes for Rh1 (the most abundant particle size) are shown in Fig. 2. The change of particle size as a function of NA is very small, but on the other hand it is significant as a function of peptization temperature. It can be concluded that at this level of WA, the influence of temperature is dominant over that of the NA.

In these set of experiments, bimodal-sized sols were obtained at 90°C . Particle sizes for the second peak varied from 70 to 30 nm as NA increased. Bimodal-sized sols were also obtained at high NA at 50°C , with similar sizes.

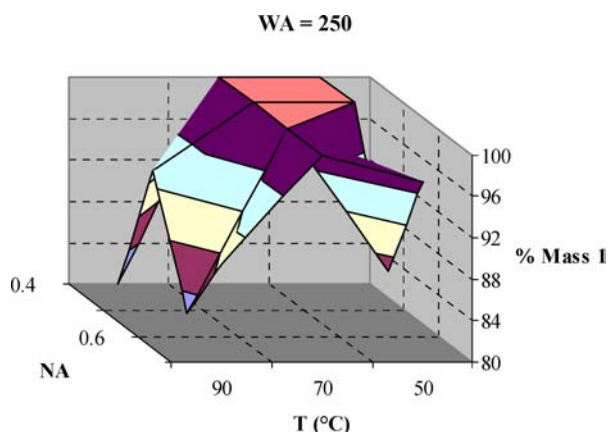


Figure 1 Graph showing optimum conditions of T and NA to obtain monomodal-sized sols prepared with WA = 250.

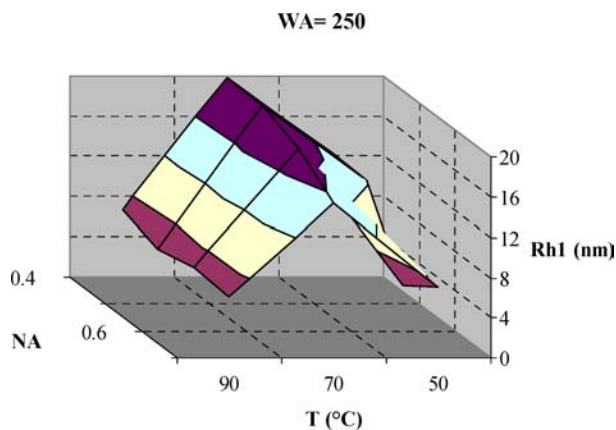


Figure 2 Graph showing Rh1 for the variation of NA and T for sols prepared with $WA = 250$.

A bimodal-sized sol most likely results at high peptization temperatures because the sol particles will have higher kinetic energy, enabling them to overcome the repulsive energy barrier. This will lead to the colliding particles falling into an energy trap of attractive forces caused by van der Waals attractions, thus leading to agglomeration of the primary particles. A similar effect can be seen when adding too much acid, since the double layer will be compressed so much that it will diminish the interparticle distance, also leading to colliding particles falling into an energy trap of attractive forces.

4.1.2. Sols prepared with $WA = 500$

A graph showing the combined effect of NA and T on % Mass 1 is shown in Fig. 3. In this case, it can be seen that peptizing at 50–70°C produced monomodal-sized sols irrespective of the NA value. However the monomodal-size sol collapsed when peptizing at 90°C, for the reasons explained above.

Particle sizes for Rh1 are shown in Fig. 4, and for this particular dilution it can be seen that the change in particle size from 50 to 70°C was considerable (from 10 to 20 nm), and was monomodal, offering a range of reaction conditions for the production of sols of predefined particle size. With respect to Rh2, similar behaviour to that observed previously was obtained. Bimodal-sized

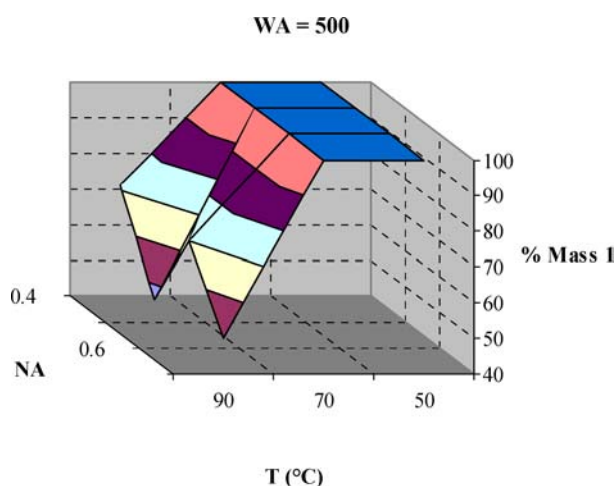


Figure 3 Surface graph showing optimum conditions of NA and T to obtain monomodal-sized sols prepared with $WA = 500$.

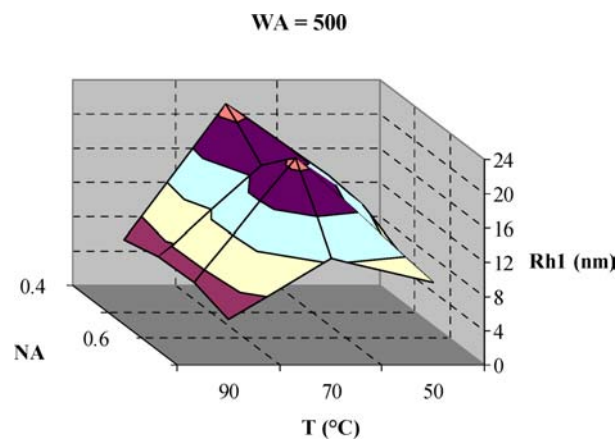


Figure 4 Graph showing Rh1 values for the variation of NA and T for sols prepared with $WA = 500$.

sols were only obtained at 90°C, the particle size for Rh2 was approximately 40–50 nm and both fractions represented a similar amount of material.

4.1.3. Sols prepared with $WA = 1000$

A graph showing the combined effect of NA and T on % Mass 1 is shown in Fig. 5. In this case, it can be seen again that peptizing at 50–70°C with NA values of 0.4 to 0.7 yielded to monomodal-sized sols. Corresponding particle sizes for Rh1 are shown in Fig. 6, which showed

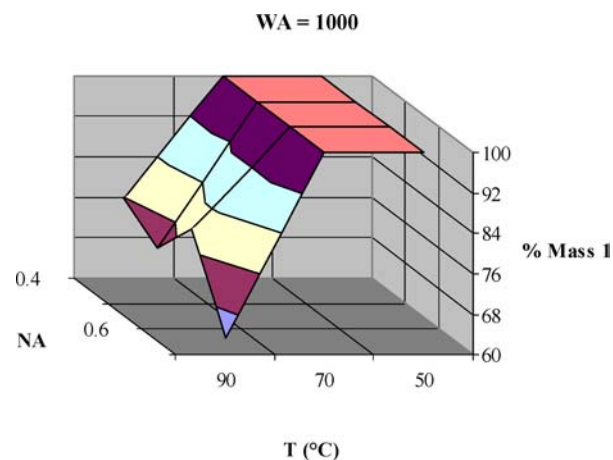


Figure 5 Surface graph showing optimum conditions of NA and T to obtain monomodal-sized sols prepared with $WA = 1000$.

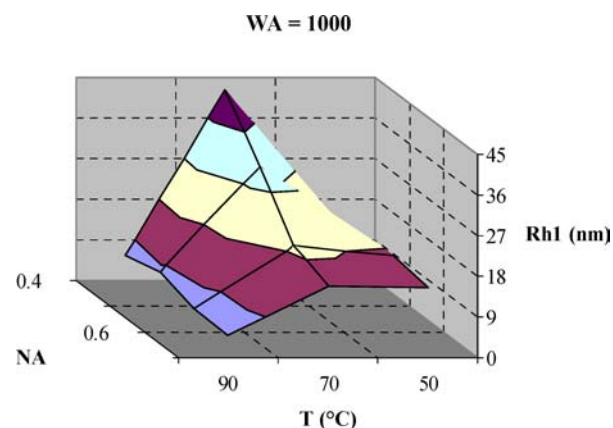


Figure 6 Surface graph showing Rh1 values for the variation of NA and T for sols prepared with $WA = 1000$

a pronounced change in particle size as a function of NA for $T = 70^\circ\text{C}$. As will be discussed later, it was under these conditions that the influence of NA was most noticeable. With respect to Rh2, again similar behaviour to that observed previously was obtained. Bimodal-sized sols were only obtained at 90°C , the particle size for Rh2 was approximately 30–50 nm, and both fractions represented similar amount of material. \sphericalangle

4.2. Stability of the sol

The stability of the sols was assessed by how thick a precipitate (if any) had formed on the bottom of the sample bottles after a five month period. It was found that the stability of the sols were dependent on the peptization temperature and pH. Stable sols were produced after peptizing at 50°C irrespective of the pH. At 70°C stable sols were formed if the pH was below 1.7 and significant precipitation was observed under the two least acidic conditions used (WA ratio of 1000 and the NA ratio ≤ 0.5). There was also significant precipitation when the sols were peptized at 90°C , the only exception to this was when the acidity of the reaction mixture was close to 1.0 (WA ratio of 250 and NA ratio ≥ 0.6). These observations can be explained by considering the competing effects of increased peptization temperature and lower pH. Higher temperatures increased the kinetic energy of the particles, making it more probable that colliding particles will overcome the energy barrier of repulsion and fall into an energy well of attraction, thus forming agglomerates. To overcome this effect a lower pH is required to maintain sufficient charge on the particles to keep them from agglomerating.

4.3. X-Ray diffraction

4.3.1. Qualitative analysis

It can be clearly seen from the diffractograms shown in Fig. 7 that all of the samples have a highly nanocrystalline nature with broad peaks. There are only three

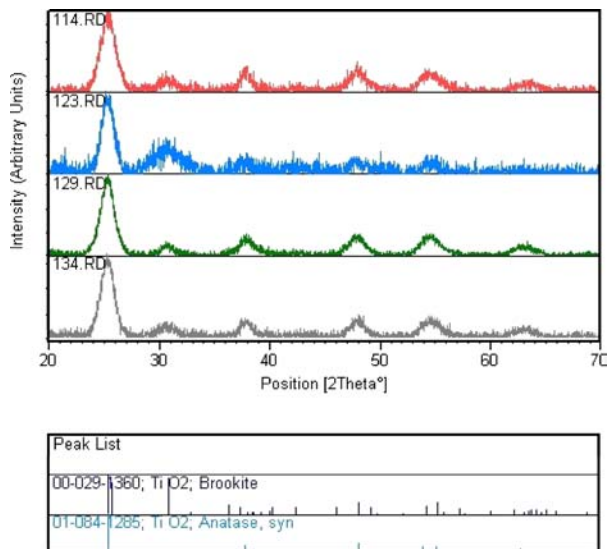


Figure 7 X-Ray Diffractograms showing the results of qualitative phase analysis for selected samples: 114 (WA = 500, NA = 0.50, $T = 50^\circ\text{C}$); 123 (WA500, NA = 0.60, $T = 90^\circ\text{C}$); 129 (WA = 1000, NA = 0.40, $T = 70^\circ\text{C}$); 134 (WA = 1000, NA = 0.50, $T = 90^\circ\text{C}$).

possible crystalline forms likely to be present in the powder: brookite, anatase and rutile. The reflections of the possible crystalline forms in the sample are presented in Fig. 7, together with reference patterns for the titania phases.

The peak of maximum intensity for rutile is located at an angle 2θ of 27.5° , and as can be seen in Fig. 7, no peak was obtained for that reflection. This was expected as a rutile phase is normally obtained at temperatures higher than 600°C . The peak of maximum intensity for both brookite and anatase is located at an angle 2θ of 25.5° , and the second highest peak for brookite is located at an angle 2θ of 30.9° . Both are the main reflections obtained in the diffractogram shown in Fig. 7. It can be concluded that the sols are mainly a mixture of brookite and anatase.

Based on qualitative assessment of the relative intensities of the brookite reflection $2\theta = 30.9^\circ$ (shown in Fig. 7), it was determined that sample 123, peptized at 90°C , WA = 500 and NA = 0.60 was the one with the highest brookite content. These results agree with the work of Wook *et al.* [15], who prepared sols with WA = 200, NA = 0.67. They found that at room temperature, mainly brookite and anatase were obtained, with some content of rutile, results that were confirmed both by XRD and Raman spectroscopy. In a different study, Hanley *et al.* [16] prepared films from sols produced at WA = 44, NA = 0.1 and $T = 70^\circ\text{C}$, XRD analysis of the air-dried film detected only anatase, however a high background was also obtained.

4.3.2. Crystallite size distribution

Crystallite size was calculated using the Scherrer equation for the brookite phase using the peak located at 30.9° , since this is the only one not overlapping with those of anatase, as seen in Fig. 7. Results are shown in Table II, and there was no significant difference between the sols. These values are in accordance with those estimated by Wook *et al.* [15] for brookite produced using similar WA and NA values, but at room temperature (2.4–6 nm).

4.4. TEM examinations on particle size

Two samples were analysed which had the smallest and the biggest particle size as determined by PCS. Fig. 8 shows the % volume distribution calculated from image analysis. It can be seen from Fig. 8 that sample 114

TABLE II Results of crystallite size analysis determined from Scherer's equation and XRD, compared with particle size concluded by PCS. Typical relative standard deviation (RSD) for crystallite size is 5%, for particle size is 8%, and for Mass 1 is 4%

Sample	Crystallite Size (nm)	Brookite				
		Rel. Intensity $2\theta = 31^\circ$	Rh 1 (nm)	Mass 1 (%)	Rh 2 (nm)	Mass 2 (%)
114	5.3	24.2	12.4	100.0		
123	6.3	53.6	6.5	70.0	48.1	30.1
129	5.4	16.1	42.2	100.0		
134	6.1	20.9	7.6	70.9	43.8	29.1

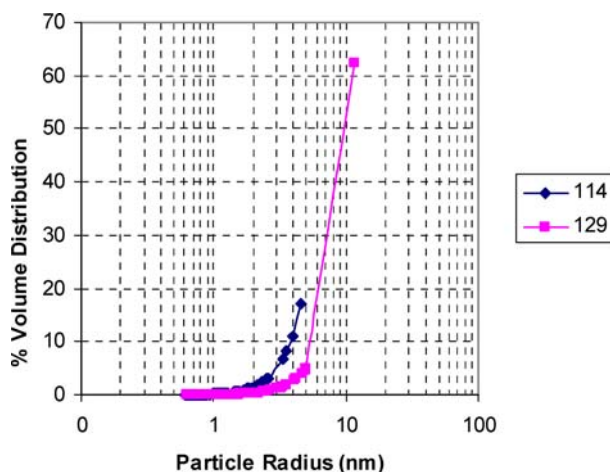


Figure 8 Volume distribution particle size by image analysis of TEM micrograph for sample 114 ($WA = 500$, $NA = 0.5$, $T = 50^\circ\text{C}$) and sample 129 ($WA = 1000$, $NA = 0.4$ and $T = 70^\circ\text{C}$).

($WA = 500$, $NA = 0.5$, $T = 50^\circ\text{C}$) had a smaller particle size than sample 129 ($WA = 1000$, $NA = 0.4$ and $T = 70^\circ\text{C}$), 4 and 10 nm respectively. This is in agreement with the PCS measurements. After similar conditions for sol preparation, but with further hydrothermal processing at 240°C , Wook *et al.* [15] reported a primary particle size of 10–15 nm (determined by TEM), a higher value than that reported here, probably due to the growth of particles during heat treatment. Similar values of 10 nm (determined by Field Emission SEM) were reported by Hanley *et al.* [16] having used the following conditions: $WA = 44$; $NA = 0.1$; $T = 70^\circ\text{C}$.

Particle size results obtained by these limited number of experiments are not expected to be representative of the samples (see the work of Jillavenkatesa *et al.* [17] regarding particle size analysis by microscopy techniques), however they are valuable in verifying the particle size measurements by PCS.

4.5. Summary

4.5.1. Keeping WA constant

Regarding peptization temperature, generally speaking, for any given WA value, the higher the peptization temperature the bigger the particle size. At $T = 90^\circ\text{C}$ all sols were bimodal and, except for sample 104 ($T = 50^\circ\text{C}$ and $NA = 0.7$), $Rh2$ values were the biggest obtained from all the set of conditions, although $Rh1$ values for these conditions were the smallest. This trend agrees with the DLVO theory in the fact that an increase in the peptization temperature leads to an increase in the kinetic energy of the particles, increasing therefore the probability for them to collide and agglomerate. The trend also agrees with the study of Vorkapik and Matsoukas [11], however a direct comparison of values cannot be made due to the fact that neither gave information on the polydispersity of the sample.

4.5.2. Keeping T constant

It can be seen that in the range 50 – 70°C , the general trend is that the higher the WA value, the higher the

$Rh1$ value, a behaviour that is more pronounced at $T = 70^\circ\text{C}$ and $NA = 0.4$. This trend however is inverted at $T = 90^\circ\text{C}$ for $Rh2$, whereas $Rh1$ remains unaffected. For $T = 50^\circ\text{C}$, Rh varies only from 10 to 20 nm, whereas for $T = 70^\circ\text{C}$ Rh varies from 10 to 40 nm, although the latter sols had more precipitation. A definitive trend therefore cannot be established. Barringer and Bowen [4] found a tendency of reduced particle size by increasing WA , however they used far more concentrated sols (WA values in the range 2–7) than the ones studied in this project. Kato's results [18] show the same tendency mentioned by Barringer and Bowen [4], unfortunately particle size measurements were not carried out and therefore a valid comparison cannot be made.

The diluted concentrations used in the present project suggest that NA values are more important in determining the final properties of the sol than the WA values.

4.5.3. Keeping T and WA constant

Regarding the NA value, it was found that it did not have a considerable influence on $Rh1$ at $T = 50^\circ\text{C}$. For $T = 70^\circ\text{C}$ and $WA = 1000$ $Rh1$ reduced with increasing NA . This suggests more powerful peptization conditions yielding smaller particle sizes. Similar findings were reported by Vorkapik and Matsoukas [11] who described the same behaviour in the $[\text{H}^+]/[\text{Ti}]$ ratio range of 0–0.5 (optimum condition) before producing unstable sols due to an excess of acid. The greatest influence of NA was seen at $T = 90^\circ\text{C}$ where, although $Rh1$ remained constant, there were large changes to $Rh2$ due mainly to the high temperature.

5. Conclusions

For the conditions investigated, stable monomodal-sized sols were obtained at $T = 50^\circ\text{C}$ (for any WA/NA ratio) and at $T = 70^\circ\text{C}$ when the pH was <1.7 . At higher temperatures the acidity of the peptising solution had to be close to 1.0 to yield a stable sol. Conditions are reported for stable, monomodal sols with average particle sizes from 6 to 40 nm. In general peptizing at 70°C resulted in larger particles than at 50°C and the less acidic the conditions were the larger the particle size.

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