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Stability of zircon pigments in water and diethylene glycol media: The case of turquoise V–$ZrSiO_4$

Sema Akdemir, Emel Özel*, Ender Suvacı

Department of Materials Science and Engineering, Anadolu University, 26480 Eskisehir, Turkey

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Abstract

The stability of pigment particles can be affected by physico-chemical interactions between the pigment particles and a solvent. In this study, the surface charges and stabilities of blue V–$ZrSiO_4$ pigments in aqueous (water) and non-aqueous (diethylene glycol) suspensions were investigated. As a function of pH, the isoelectric points (IEP) for the commercial and synthesised pigments were determined to be 2.2 and 1.7, respectively. ICP-OES results show that the cations of V–$ZrSiO_4$ pigments dissolve in both aqueous and non-aqueous systems. The dissolution of the pigment particles was more significant in DEG because the total ion concentration (>2000 ppm) was higher than that of the aqueous medium (>200 ppm). The colour stability of the V–$ZrSiO_4$ powder deteriorates as a consequence of an insufficient chemical stability both in the water and DEG media. Additionally, the V–$ZrSiO_4$ particles dissolve with proton-promoted and hydroxyl-promoted dissolution mechanisms in the aqueous medium, whereas these particles dissolve with a ligand-promoted dissolution mechanism in the non-aqueous medium.

Keywords: A. Suspension; C. Colour; Silicates; Pigments

1. Introduction

Ceramic pigments are important materials used to introduce colour into ceramic bodies and glazes. Zircon ($ZrSiO_4$) pigments are commonly used in the ceramic industry due to their superior thermal and chemical stabilities. When praseodymium, vanadium or iron ions are introduced into the zircon lattice, the colour of the zircon pigments are yellow, blue or pink, respectively. For a blue colour, V–$ZrSiO_4$ has been widely used in the ceramic industry for several decades. It is accepted that the origin of the blue colour in this pigment is due to the solid solution of V^{+4} in the zircon lattice [1–3].

The use of new decoration techniques is becoming increasingly more popular in the ceramic tile industry to provide the production of high-quality images on tile surfaces. Among those techniques, ink-jet printing is the most promising technology to achieve this aim. Nevertheless, ink-jet printing has some requirements, such as using submicron pigment particles. The submicron pigment particles provide increased scattering and higher absorption, which improve colour strength. However, increasing the surface area of the pigment particles causes stabilisation problems in dispersed media [4,5], where the stability of the pigment is affected by the physico-chemical interactions between the pigment particle and the solvent.

An oxide surface has two main groups: Bronsted and Lewis acid sites. Bronsted acids are defined as proton donors, such as M–OH sites on oxide surfaces. Lewis acids are defined as electron-deficient, or will accept an electron pair, such as M^+ and/or $M(OH)_2^+$ [6,7]. In acidic media, the detachment of the metal ions occurs after sufficient proton adsorption onto the Bronsted acid sites of the oxide surface, which is denoted as a proton-promoted dissolution mechanism. Alternatively, in basic media, OH^- behaves similar to a ligand, encouraging oxides to dissolve and form alkali complexes. These complexes polarise the metal–oxygen bonds, resulting in a detachment of the metal ion from the oxide surface [8].

In non-aqueous media, the chemical interactions and adsorption mechanisms of different oxide surfaces have

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*Corresponding author. Tel.: +90 222 3213550x6372; fax: +90 222 3239501.
E-mail address: eozel@anadolu.edu.tr (E. Özel).

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been reported. Mathur and Moudgil studied the adsorption behaviour of polyethylene oxide (PEO) on oxide surfaces and suggested that adsorption of PEO onto an SiO_2 surface occurred via hydrogen bonding [9]. Additionally, Saravanan and Subramanian used a similar argument for the adsorption of PEO, which is also known as PEG, onto zirconia [6]. The ether oxygen of PEO interacts with a Bronsted acid site (M–OH) via hydrogen bonding. Higher adsorption of PEO onto oxide surfaces is dependent on the Bronsted acidity of the oxide, where the Bronsted acidity can be explained by the ratio of the cationic charge to the radius (Z/r). Higher Z/r provides a higher acidity and thus a lower IEP. In other words, an oxide with a low IEP has a higher Bronsted acidity, that is, PEO interactions with M–OH groups [9].

Although many studies have reported on the stabilities of pigment particles [10,11] and oxide powders [12,13] in aqueous suspension, to our knowledge, the stability of the V–$ZrSiO_4$ blue pigment powder in aqueous and non-aqueous media has not been previously reported in the literature. Accordingly, the research objective of this study was to investigate the interactions between the V–$ZrSiO_4$ particles and the different solvents depending on their pH and particle size. Therefore, an understanding of these interactions with V–$ZrSiO_4$ will be essential for the preparation of pigment suspensions that are used as ink.

2. Experimental procedures

2.1. Raw material characterisation

Commercially available V–$ZrSiO_4$ pigment was supplied by Colorobbia (Spain), but it is important to distinguish between the commercial and synthesised pigment powders. Pure V–$ZrSiO_4$ pigment powder was synthesised by a solid-state reaction from a mixture of pure zirconia (ZrO_2, Riedel Haen), silica (SiO_2, Riedel Haen) and ammonium metavanadate (NH_4VO_3, Merck) at 1100 °C for 3 h. Sodium fluoride (NaF, Merck) was used as a mineraliser. To identify the crystalline phases present in the pigments, X-ray diffraction (XRD, Rigaku Rint 2200, Japan) patterns were obtained using conventional powder diffraction with CuKα radiation and a goniometer speed of 2°/min. The chemical analysis of the pigment powder was carried out via X-ray fluorescence (XRF, Rigaku ZSX Primus, Japan).

A laser diffraction method (Mastersizer 2000, UK) was used to determine the average particle sizes of the commercial and synthesised pigments, which were found to be 5.7 and 3.9 μm, respectively. To understand the effect of the particle size on the dissolution behaviour of V–$ZrSiO_4$, the pigment powder was ground to achieve particle sizes of 1 μm and 500 nm using an attrition mill at 450 rpm with yttria-stabilised zirconia balls in an isopropyl alcohol medium.

2.2. Suspension characterisation

The chemical stability of the V–$ZrSiO_4$ blue pigment particles was investigated based on the pigment particle size, pH and solvent (media). Distilled water and diethylene glycol (DEG, PETKİM Petrokimya AŞ) were used as the media. Suspensions were prepared by adding 5 wt% of the pigment powders to either the distilled water or the DEG. All the suspensions were magnetically stirred in a polyethylene (PE) bottle and ultrasonicated to achieve a thorough dispersion of the particles. The pH of the suspensions in the aqueous medium was measured to be 9 with a pH metre (Thermo Scientific Orion 4 Stars, USA). Alternatively, the suspension pH was adjusted by adding HCl and NH_4OH to the distilled water to obtain a pH of 7 and a pH of 11, respectively, to investigate the effect of the pH on the chemical stability of the pigment suspensions.

To determine the isoelectric point (IEP) of both the commercial and synthesised V–$ZrSiO_4$ pigment systems, zeta potential measurements (Zetasizer NanoZS, Malvern, UK) as a function of pH were performed. For the zeta potential measurements, both the commercial and synthesised V–$ZrSiO_4$ pigment suspensions were prepared by adding 1 g of the pigment powder to 100 ml of distilled water. All suspensions were homogenised by magnetic stirring and ultrasonication.

The type and concentration of ions dissolved in both the aqueous and non-aqueous solutions were determined using inductively coupled plasma optic emission spectroscopy (ICP-OES, Varian, USA). The suspensions prepared with 5 wt% pigment powders were centrifuged at 3000 rpm for 10 min (Universal 32, Hettich, USA). Then, 10 ml of the supernatant part of the suspensions was collected for the first 10 h at 1-h intervals and for the following 7 days in 24-h intervals. The collected supernatants were characterised via ICP-OES.

2.3. Colour measurements

To understand the effect of the aging process on the colour properties of the pigment powders in different media, the powders in the suspensions were dried. After 100 h, the colour stability was evaluated by measuring the CIEL*a*b* parameters of the aged pigments using a spectrometer (Konica Minolta CM3600 d, Japan, illuminant D_{65}, 10° observer). The colour properties of the aged pigments were compared with those of the untreated pigments in the form of ΔE. ΔE is a measurement used to indicate how much the measured colour deviates from a standard. A higher ΔE indicates a larger deviation from the original colour.

3. Results and discussion

3.1. Characterisation of pigment powders

Fig. 1 shows the typical XRD patterns of both the commercial and synthesised V–$ZrSiO_4$ pigments. The XRD

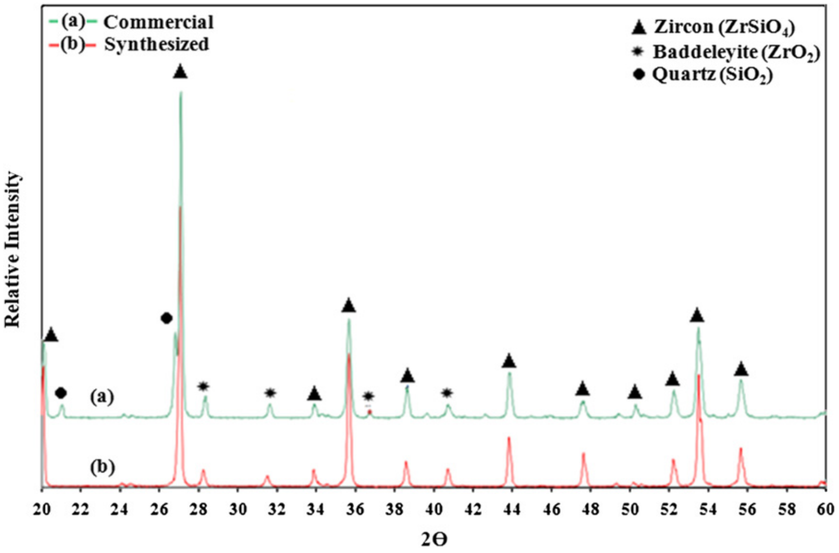

Fig. 1. XRD patterns of the commercial and synthesised V–$ZrSiO_4$ pigment powders.

Table 1
Chemical analysis of pigment powder with XRF.

	Oxides (wt%)				
	Na_2O	SiO_2	ZrO_2	V_2O_5	HfO_2
Commercial	1.50 ± 0.01	43.00 ± 0.01	52.00 ± 0.01	2.40 ± 0.01	1.10 ± 0.01
Synthesised	2.60 ± 0.01	29.50 ± 0.01	63.30 ± 0.01	3.40 ± 0.01	1.20 ± 0.01

pattern of the synthesised V–$ZrSiO_4$ pigment powder presents zircon ($ZrSiO_4$) and baddeleyite (ZrO_2) phases. However, the commercial V–$ZrSiO_4$ pigment powder exhibits zircon ($ZrSiO_4$), baddeleyite (ZrO_2) and a low amount of quartz (SiO_2) phases. The chemical composition of the V–$ZrSiO_4$ pigment powders is listed in Table 1. The commercial pigments contain a higher amount of SiO_2 than the synthesised pigments, indicated by the quartz phase content.

The electrokinetic behaviour of the V–$ZrSiO_4$ pigment as a function of pH is shown in Fig. 2. The net charge of the particle surface, which is called the isoelectric point of charge (IEP), is zero at a certain pH. The IEP of the commercial and synthesised V–$ZrSiO_4$ pigments were 2.2 and 1.7, respectively. Small variations in the IEPs between the commercial and synthesised pigments can be attributed to an excess of the quartz phase in the commercial pigments. Because the IEP of quartz has a pH of 2–3 [14], it can be concluded that the excess quartz (SiO_2) phase in the commercial pigment powder causes a small increase in the IEP. The zeta potential values of the pigment particles range from $+10$ mV to -70 mV. At a pH below or above the IEP, the particle's surfaces become positively (M–OH^{+2}) or negatively (M–O–) charged due to the addition of either an acid (H^+) or a base (OH^-), respectively [15–17]. Accordingly, the surface charge of V–$ZrSiO_4$ pigment particles in an aqueous medium becomes gradually more negative at higher pH values. The particles with low zeta potentials ($< \pm 30$ mV) experience a minimised electrostatic repulsion, which makes the suspension unstable [6,15–17]. Therefore, it can be concluded that V–$ZrSiO_4$ suspensions are more stable at higher pH values from Fig. 2.

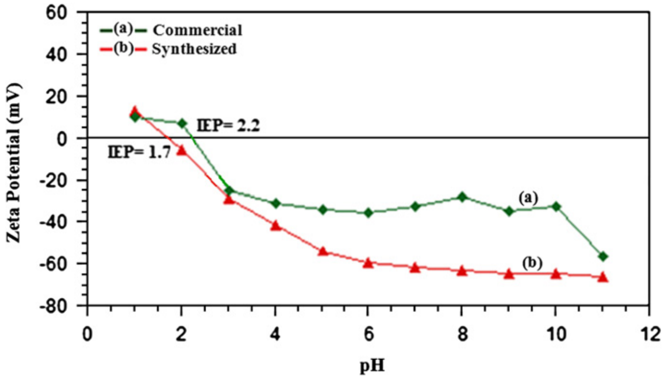

Fig. 2. Evaluation of the zeta potential of the commercial and synthesised V–$ZrSiO_4$ pigment powders in water as a function of pH.

3.2. Suspension characterisation in an aqueous medium

Two types of the same pigment were studied to distinguish the difference between the commercial and synthesised pigment powders. The commercially available V–$ZrSiO_4$

pigment, supplied by Colorobbia (Spain), contains different phases: zircon, baddeleyite (ZrO_2) and quartz. These phases make the chemical interactions between the pigment powder and the medium more complex. Therefore, the dissolution phenomenon was clarified using the synthesised V–$ZrSiO_4$ pigment, which has no quartz phase.

In commercial pigments, zirconium ions are present in both the zircon and baddeleyite phases. Korhinskaya reported that the concentration of zirconium ions in the equilibrium solution with zircon and quartz is 1–1.5 orders of magnitude higher than the concentration in a solution with baddeleyite. The solubility of baddeleyite in pure water and in diluted solutions of HCl is insignificant when compared with the solubility of zircon and baddeleyite with the same T–P–mHCl conditions [18]. Therefore, the zirconium ions in an aqueous solution were primarily contributed from the zircon phase, rather than the minor contribution of the baddeleyite phase.

The effect of the particle size on the dissolution of the commercial pigment particles in aqueous media at a pH of 9 for all ions is shown in Fig. 3. Generally, ion concentrations in suspensions increase with a decreasing particle size, from 5.7 μm to submicron sizes. The Zr^{4+} ion concentration reaches a maximum of 200 ppm for a particle size of 500 nm. Unexpectedly, the ion concentrations are lower for the 500-nm particles than the 1-μm particles, but higher for the 5.7-μm particles. Because the reactivity of the particles increases with increasing surface area, the dissolution rate of the submicron pigment particles in an aqueous medium is higher than the rate for the micron pigment particles.

The dissolution behaviour of the commercial V–$ZrSiO_4$ pigments in water was examined for pH values of 7, ~9 (natural pH) and 11. Fig. 4 shows the ion concentrations for commercial V–$ZrSiO_4$ pigments (500 nm) at different pH values. At pH 7, the concentrations of the ions in the suspensions were ~17 ppm for Si^{4+}, ~2 ppm for V^{4+} and <1 ppm for Zr^{4+} ions. However, the Zr^{4+} and Si^{4+} concentrations increased significantly with increasing time when the pH increased to 11 (Fig. 4c). The Zr^{4+} and Si^{4+} concentrations reached 250 and 140 ppm, respectively, after 120 h. The results show that the dissolution becomes more significant at higher pH values, excluding V^{4+}. Under alkaline conditions, the hydroxyl-promoted dissolution mechanism is dominant [6,7]. According to the results in this study and those reported in the literature, the V–$ZrSiO_4$ blue pigments dissolve with proton-promoted and hydroxyl-promoted dissolution mechanisms in aqueous media when pH < IEP and pH > IEP, respectively.

Fig. 5 shows the different dissolution behaviours of the synthesised and commercial pigments having 1-μm particles at pH 9. The dissolution degree of V^{4+} and Zr^{4+} in the commercial pigment (~180 ppm) is lower than that of the same conditions with the synthesised pigment (~270 ppm). Therefore, the quartz particles in the commercial pigment influence the dissolution behaviour, leading to a decrease in the solubility of zircon, as reported in a previous study [19]. Additionally, a higher Si^{4+} concentration was observed for the commercial pigment (Fig. 5), indicating that the silicon ions came from both the zircon and quartz phases, with the quartz phase contributing more to the concentration values.

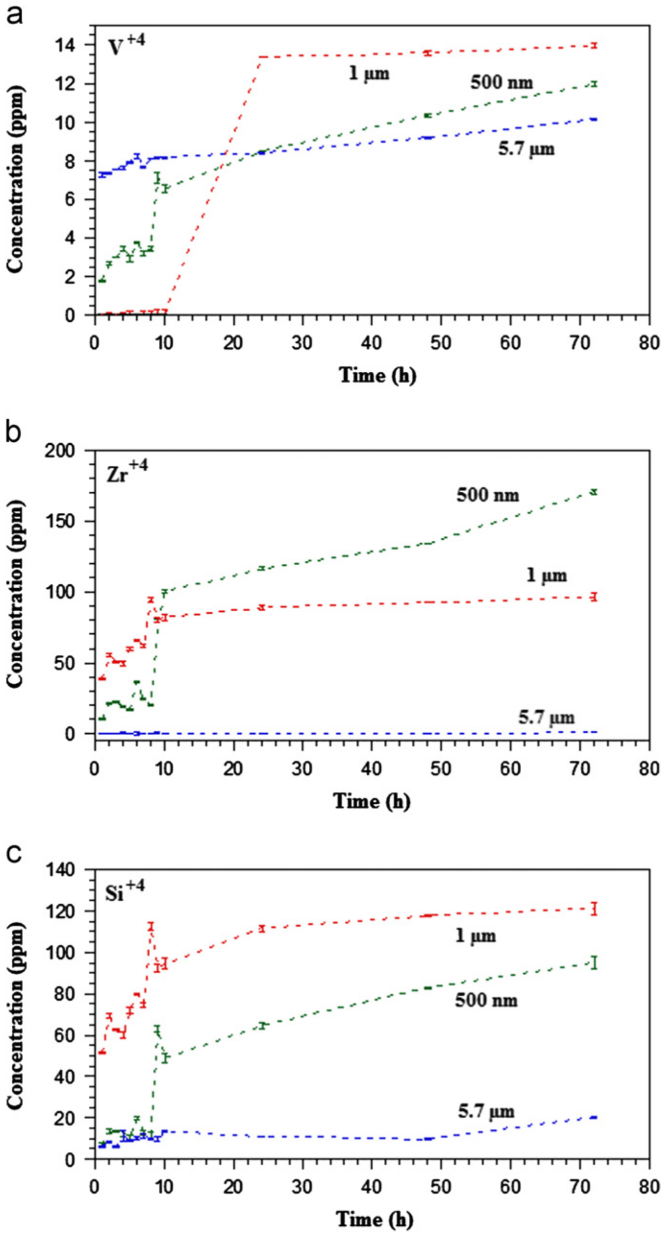

Fig. 3. Effect of the particle size on the dissolution of the commercial V–$ZrSiO_4$ pigment at pH 9 for (a) V^{4+}, (b) Zr^{4+} and (c) Si^{4+}.

The dissolution process of quartz in water has been well researched, including results under various conditions, such as the temperature, pH or concentration of background electrolytes [20–23]. The surface hydrolyses to form hydroxide layers (Si–OH) when the quartz particles are immersed in water, and the water molecules react with the silicon oxide or hydroxide surface. Hydroxide (Si–OH) surfaces adsorb protons (H^+ ions) at low pH values to produce positively charged surfaces (Si–OH_2^+) but lose their protons at higher pH values to produce negatively charged surfaces (Si–O^-) [24]. Degen and Kosec emphasised that solubility of oxides

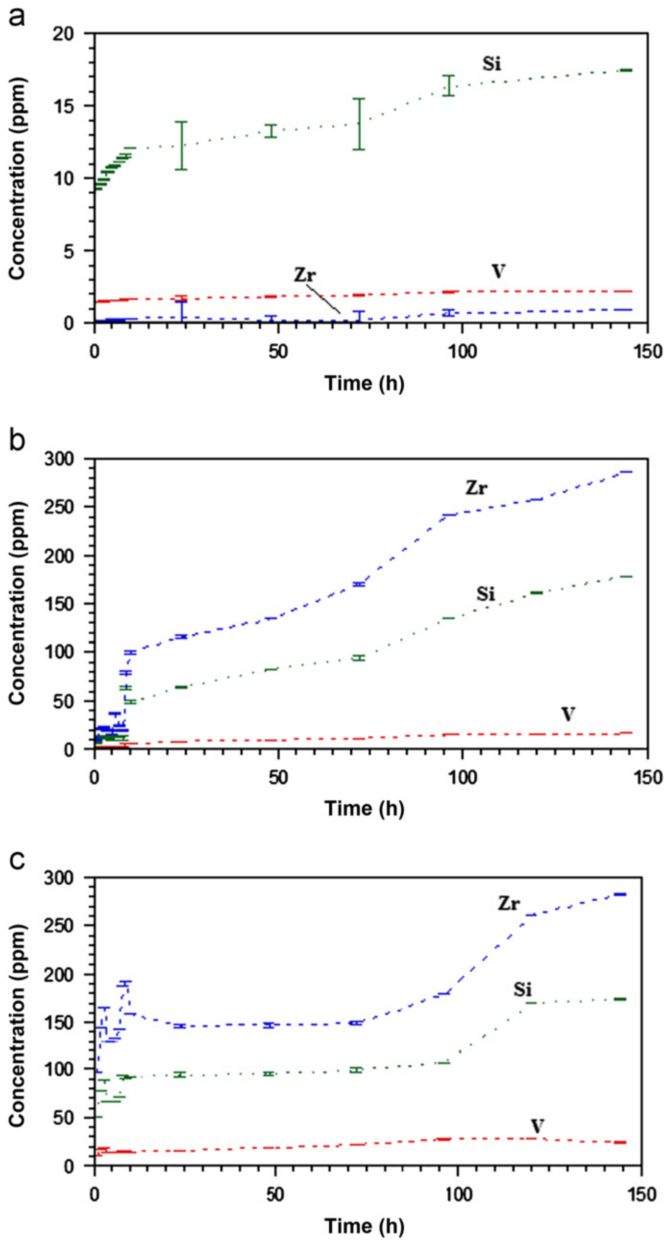

Fig. 4. Ion concentration of the commercial V–$ZrSiO_4$ pigment (500 nm) at (a) pH 7, (b) pH 9 and (c) pH 11.

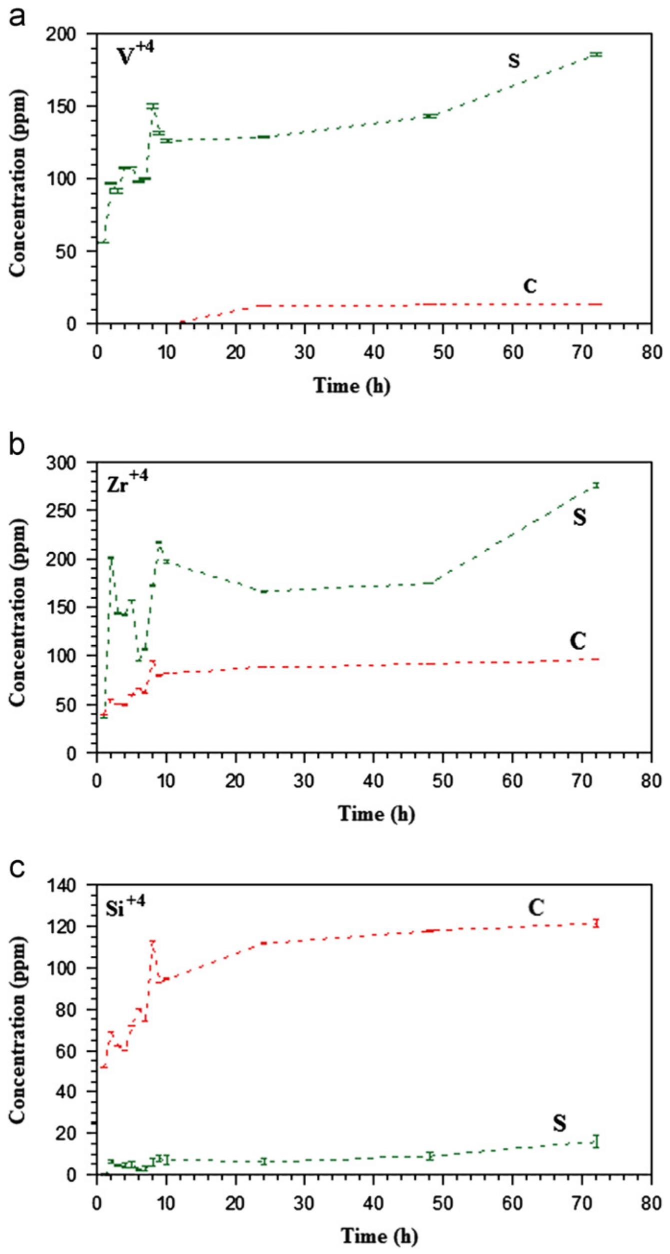

Fig. 5. Ion concentrations for the commercial (C) and synthesised (S) pigment powders (1 μm) at pH 9 in an aqueous medium.

was strongly dependent on the pH, especially when the cation can form hydroxyl complexes [25]. Zirconium ions in a solution tend to hydrolyse and complex with anions due to a high charge, small radius and comparatively small ionisation [16]. Although the chemical behaviour of zirconium in water solutions containing different cations has not been clearly understood [26], it can be concluded that the dissolution rate of the zircon was affected by the silicon-based hydroxyl complexes, which were present in aqueous solutions.

3.3. Suspension characterisation in a non-aqueous medium

The interaction between the pigment particles and the DEG medium is shown in Fig. 6. Both the commercial and synthesised pigment powders exhibit higher ion concentrations (>500 ppm) in the non-aqueous medium after 70 h than in the aqueous medium (<200 ppm, shown in Fig. 5). The V^{4+} concentration was detected at approximately 2000 ppm for the synthesised pigment powder, although the commercial powder concentration was 100 ppm (Fig. 6a). The dissolution of V^{4+} in the DEG medium is suppressed by excess Si^{4+} that result from the quartz particles, similar to the case of water. The zirconium ion concentration was high (i.e., 1200 ppm) in both commercial and synthesised pigment systems (Fig. 6b), whereas only the commercial pigment powder system in the DEG medium had Si^{4+} concentrations exceeding 1000 ppm with increasing time (Fig. 6c).

Generally, the dissolution rate of all ions drastically increases in DEG compared with the results in the aqueous system. The adsorption of DEG onto an oxide surface can be explained by a Lewis acid–base interaction and hydrogen bonding with a Bronsted acid site [6,7]. However, the adsorption in the non-aqueous system can only be observed via the Lewis acid–base interaction due to the absence of water. For this reason, the DEG chain behaves in the following manner: it selectively attacks the Lewis acid site (M^+), depending on the coordination number of the cation that provides information about ligands; next, it covalently bonds to the central atom and weakens the metal–oxygen bond, and finally, it results in a facilitated dissolution of the pigment cation into the non-aqueous suspension.

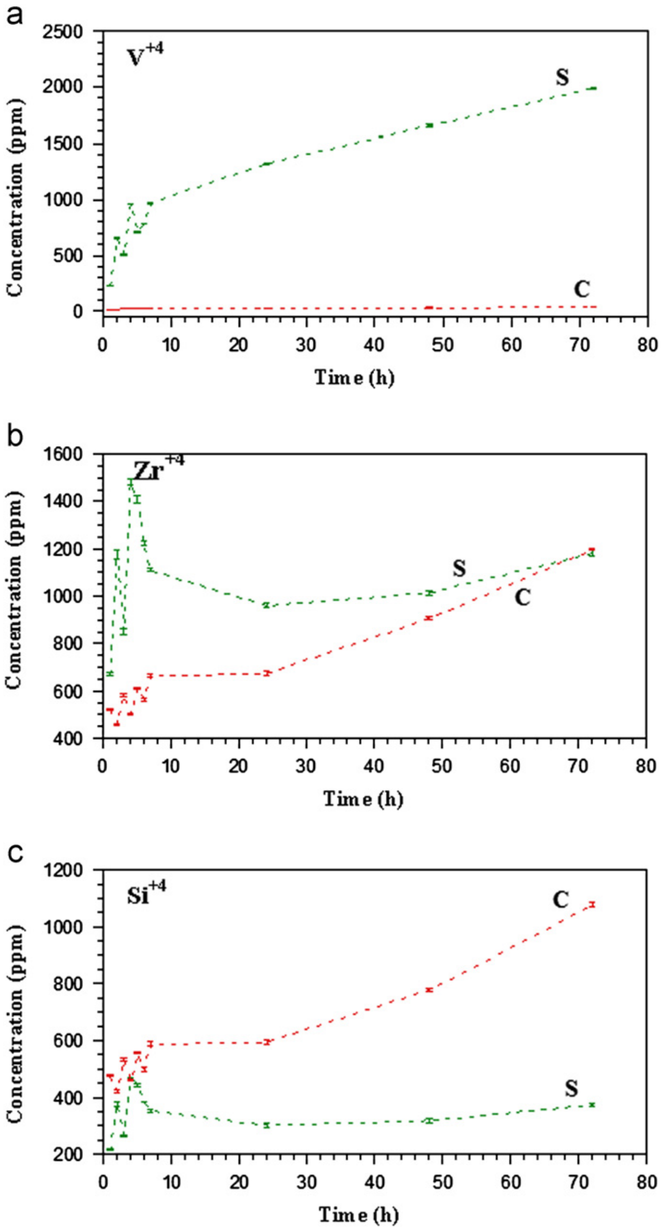

Fig. 6. Ion concentrations for the commercial (C) and synthesised (S) pigment powders (1 μm) in the DEG medium.

3.4. Colour properties of pigments

The colour properties of the untreated pigments and the aged pigments obtained from suspension after 100 h are presented in Table 2. The total colour difference, ΔE (the total difference or distance on the CIELAB diagram at ΔL^*, Δa^* and Δb^* values), between the untreated and aged commercial pigment powders in water was 4.18, whereas ΔE was 6.90 for the synthesised pigments in water. Similar colour changes were also observed for the aged pigments in DEG. When $\Delta E > 1$, the differences can be easily distinguished by the human eye. Therefore, variations in the colour properties of the aged pigments are the evidence for the deterioration in the colour stability, depending on the dissolution of the pigment particles. Pigments must be completely insoluble in their media to ensure long-term colour uniformity. A lower amount of V–$ZrSiO_4$ pigment dissolution, on the ppm level, occurred in both media. These ceramic pigment suspensions cannot be stored in the long term due to the colour change that is dependent on the dissolution of pigment cations in the aqueous and non-aqueous media. For this reason, the results of this study can be utilised to develop stabilisation strategies for the pigments in aqueous and non-aqueous media.

4. Conclusions

In this study, the physico-chemical behaviour of the ceramic V–$ZrSiO_4$ pigment in aqueous and non-aqueous media was investigated as a function of particle size and solution pH. Dissolution of the V–$ZrSiO_4$ pigment particles is more prominent at a higher pH and a smaller particle size. Because the pigment cations have a higher dissolution rate in the non-aqueous medium than in the aqueous medium, the colour uniformity deteriorates

Table 2
Colour properties of pigments after aging for 100 h in water and DEG.

Media	L^*	a^*	b^*	c^*	h	ΔE^*
Untreated commercial pigment	67.78 ± 0.01	-14.18 ± 0.01	-15.47 ± 0.01	20.99 ± 0.01	227.49 ± 0.01	
Aged pigments in water	63.68 ± 0.01	-14.93 ± 0.01	-15.34 ± 0.01	21.41 ± 0.01	225.77 ± 0.01	4.18
Aged pigments in DEG	65.59 ± 0.01	-15.21 ± 0.01	-16.71 ± 0.01	22.60 ± 0.01	227.70 ± 0.01	2.72
Untreated synthesised pigment	76.32 ± 0.01	-13.32 ± 0.01	-14.26 ± 0.01	19.51 ± 0.01	226.96 ± 0.01	
Aged pigments in water	70.15 ± 0.01	-14.35 ± 0.01	-17.17 ± 0.01	22.38 ± 0.01	230.10 ± 0.01	6.90
Aged pigments in DEG	72.95 ± 0.01	-15.06 ± 0.01	-18.27 ± 0.01	23.68 ± 0.01	230.50 ± 0.01	5.52

considerably in the non-aqueous medium. The quartz phase in commercial pigments provides a lesser colour change by reducing the dissolution of vanadium and zirconium ions in both the water and DEG media.

According to the results here and in the literature, it can be concluded that the V–$ZrSiO_4$ pigment particles dissolve with proton-promoted and hydroxyl-promoted dissolution mechanisms in an aqueous medium, whereas the V–$ZrSiO_4$ pigment particles dissolve as a consequence of the ligand-promoted dissolution mechanism in a non-aqueous medium.

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