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Solubility of blue $CoAl_2O_4$ ceramic pigments in water and diethylene glycol media

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Abstract

The chemical stability of blue $CoAl_2O_4$ ceramic pigment in aqueous and non-aqueous suspension was investigated. Distilled water and diethylene glycol (DEG) were used as media. The isoelectric points (IEP) for the commercial and synthesised $CoAl_2O_4$ pigment were determined to be 4.9 and 8.5, respectively. The IEP shifts toward acidic pH values for the commercial pigment with respect to the synthesised pigment due to the existence of the quartz phase. In water, the cobalt ion concentration was low (2.5 mg dm^{-3}), and this concentration did not change with time. However, the aluminium ion concentration was initially high and then decreased to $\sim$10 mg dm^{-3} at pH 9 and 11 due to the precipitation of Al^{3+} ions as an $Al(OH)_3$ phase. In DEG, the dissolution of pigment particles with higher ion concentrations (>800 mg dm^{-3}) was more significant than that of the aqueous medium, implying that $CoAl_2O_4$ pigment has insufficient chemical stability in DEG medium with respect to aqueous suspensions.

Keywords: Chemical stability; Dissolution; Cobalt aluminate; Ceramic pigment

1. Introduction

Ceramic coatings are often applied over ceramic products to improve their appearance. Most ceramic coatings contain different components to provide the desired colour [1]. One of these components is the ceramic pigment, which are inorganic structures containing chromophore ions that also impart their colour to ceramic wares by forming a heterogeneous mixture with the body or glaze [2]. The origin of inorganic pigments is based on oxide structures, which are produced by solid state reactions at high temperatures. Moreover, inorganic pigments are practically insoluble in media that do not react physically/chemically with their dispersed medium [3]. $CoAl_2O_4$ pigment is widely utilised in the ceramics industry as a colouring agent in glaze and bulk tile compositions due to its superior properties, such as high refractive index, chemical and thermal stability, and colour stability [3]. In addition, $CoAl_2O_4$ pigments have an intense blue colour with a spinel structure [4].

The ceramic tile market has an increased interest in specially modified products in order to provide high-quality images on tile surfaces where the decoration has considerable qualifications [5]. Conventional screen printing methods have been used for many decades as decoration techniques that are highly efficient and practical. However, they have some considerable limitations such as cracks on green bodies and wear of screens [1]. Therefore, new printing methods such as ink-jet printing can be used to overcome these limitations and provide high quality images on ceramic tiles. Ink-jet printing has some properties that make it potentially attractive. For instance, it is a non-contact method based on projecting ink droplets onto a surface and permits better control of the image quality. Another characteristic of this method is the usage of submicron and nanosized pigment particles.

Nanosized pigments have high surface area, which produces improved scattering due to the high number of reflectance points [6]. However, using of submicron or nanosized pigment particles in ink-jet printing technology leads to stabilisation problems. On the other hand, most of the ink-jet inks are suspensions of pigments in an organic solvent, although a water-based medium provides more environmentally friendly inks. Nevertheless, under both aqueous and non-aqueous

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conditions, the ink industry faces stability issues that can have great impact on the quality of the finished product. Furthermore, although $CoAl_2O_4$ is one of the most important pigments in the ceramics industry, there is almost no report on their chemical stability in aqueous/non-aqueous media. Therefore, the aim of this research is to investigate the effect of particle size on the chemical stability of $CoAl_2O_4$ pigments in aqueous/non-aqueous media and determine the interaction between the pigment particles and medium.

2. Materials and methods

2.1. Raw materials characterisation

Industrially available $CoAl_2O_4$ pigment was supplied by Colorobbia (Spain). In addition, pure $CoAl_2O_4$ pigment powder was synthesised by mixing reagent grades of cobalt oxide (Sigma–Aldrich) and aluminium oxides (Sigma–Aldrich) and calcining this mixture at 1300 °C for 3 h to distinguish the difference between the commercial and the synthesised pigment powders. These powders were characterised by X-ray diffraction (XRD, Rigaku Rint 2200, Japan) using Cu Kα radiation. Chemical analysis of pigment powder was achieved by X-ray fluorescence (XRF, Rigaku ZSX Primus, Japan). The average particle size of the commercial pigment was measured via the laser diffraction method (Mastersizer 2000, UK) and was found to be 6 μm. The mean specific surface area of the commercial pigment powder was determined by the Brunauer–Emmitt–Teller (BET) technique (Quantochrome Autosorb-1C, USA) to be $2.54\ m^2\ g^{-1}$. Pigment powders were ground to 1 μm and 500 nm mean particle sizes in order to evaluate the effect of the particle size on pigment stability. Pigment powders are labelled based on their particle size as (1 μm) and (500 nm) throughout the text.

As received and aged pigment powders in suspension were characterised using a Fourier transform infrared (FT-IR) spectrometer (Tensor 27, Bruker, USA) in order to understand whether or not there is an interaction between pigment powders and medium. For the FTIR experiments, the pigment suspensions were dried at 100 °C in an oven, and then the dried pigment powders were mixed homogeneously with KBr. After the powders were pressed into pellets, measurements were performed.

2.2. Suspension characterisation

In order to determine the chemical stability of the $CoAl_2O_4$ blue pigment particles in aqueous and non-aqueous suspensions, distilled water and diethylene glycol (DEG) were used (Eczacibasi Vitra, Turkey) as solvents. Suspensions were prepared by adding 5 wt% pigment powder to either distilled water or DEG. The suspensions were magnetically stirred in a polyethylene (PE) bottle, and ultrasonication was also used to achieve high dispersion of the particles.

The natural pH value of suspensions in aqueous media was measured with a pH-meter (Thermo Scientific Orion 4 Stars, USA), and it was found to be 9. In addition, the suspensions in an aqueous environment were prepared at pH 7 and pH 11 by adding HCl acid and NH_4OH base solutions to the distilled water, respectively, in order to investigate the effect of pH on the chemical stability of the pigment suspensions.

For zeta potential measurements, both the commercial and the synthesised $CoAl_2O_4$ pigment suspensions were prepared by the addition 1 g of the pigment powder into $100\ cm^3$ of distilled water. All suspensions were homogenised by magnetic stirring and ultrasonication. Then, zeta potential measurements as a function of pH were carried out in order to determine the isoelectric point (IEP) of both the commercial and the synthesised $CoAl_2O_4$ pigment systems. Electrophoretic mobility measurements were performed with laser Doppler velocimetry (Zetasizer NanoZS, Malvern, UK) using the Henry equation [7], and the zeta potential values were calculated by using the following formula:

$$\mu e = \frac{2\varepsilon z f(Ka)}{3\eta} \qquad (1)$$

where μe is the electrophoretic mobility, ε the dielectric constant of medium, z the zeta potential, $f(Ka)$ the Henry function (for aqueous system $f(Ka) = 1.5$; for non-aqueous system $f(Ka) = 1$), and η the viscosity.

An inductively coupled plasma optic emission spectrometer (ICP-OES, Varian, USA) was used to determine the ion type and ion concentration in both aqueous and non-aqueous systems. In this way, the interaction between the pigment particles and medium was investigated. Accordingly, suspensions prepared with 5 wt% pigment powders were centrifuged at 3000 rpm for 10 min (Universal 32, Hettich, USA). Then, the $10\ cm^3$ supernatant part of the suspensions was collected for the first 10 h in 1-h intervals and for the following seven days in 24-h intervals. The collected supernatants were characterised by using ICP-OES.

3. Results and discussion

3.1. Characterisation of pigment powders

XRD patterns of both the commercial and the synthesised $CoAl_2O_4$ pigment are shown in Fig. 1. The synthesised

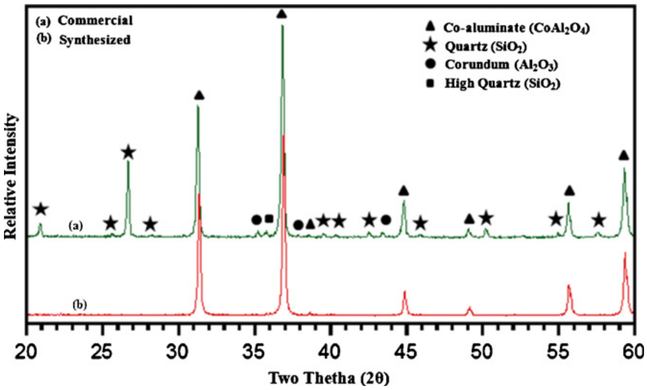

Fig. 1. XRD patterns of the commercial and the synthesised $CoAl_2O_4$ pigment.

Table 1
Chemical analysis of pigment powder with XRF.

Pigments	Oxides (wt.%)			
	Al_2O_3	Co_2O_3	MgO	SiO_2
Commercial	51.15	33.49	2.13	13.23
Synthesised	52.42	47.46	–	0.12

$CoAl_2O_4$ pigment powder consists of only the spinel $CoAl_2O_4$ phase. However, the commercial $CoAl_2O_4$ pigment powder exhibits a high amount of spinel $CoAl_2O_4$ and quartz (SiO_2) and also low amounts of residual corundum (Al_2O_3) phases. The chemical analysis of the $CoAl_2O_4$ pigment powder was performed by XRF, as shown in Table 1. The commercial pigment contains 13.2 wt% silicon dioxide (SiO_2).

3.2. Electrokinetic studies

Fig. 2 shows the electrokinetic behaviour of $CoAl_2O_4$ pigment as a function of pH. The IEPs of the commercial and the synthesised $CoAl_2O_4$ pigment were found to be pH $\cong$ 4.9 and pH $\cong$ 8.5, respectively. The differences in the IEPs of the commercial and the synthesised pigments can be attributed to the existence of the silicon dioxide (SiO_2) phase in the commercial pigment. The IEP of cobalt oxide (Co_3O_4) and aluminium oxide (Al_2O_3) are at pH $\sim$ 8 [8] and pH 8.7–9 [9], respectively, whereas the IEP of silicon dioxide (SiO_2) is at pH 1.8–2.3 [10]. Therefore, it can be concluded that the silicon dioxide (SiO_2) phase in the commercial pigment causes a decrease in IEP of the pigment powder. Surface of oxide particles generally become negatively charged above the IEP and positively charged below the IEP. The particles with low zeta potentials ($< \pm 30$ mV) result in minimised electrostatic repulsion, which make the suspension unstable [11–14]. Therefore, surface charge provides information about which type of additives (cationic or anionic) can be used at different pH values.

3.3. Suspension characterisation in aqueous medium

The commercial $CoAl_2O_4$ pigment powder has different phases. These are spinel, corundum and quartz, which make the chemical interactions between the pigment powder and medium more complex. Therefore, the dissolution phenomenon was clarified by using the synthesised $CoAl_2O_4$ pigment system.

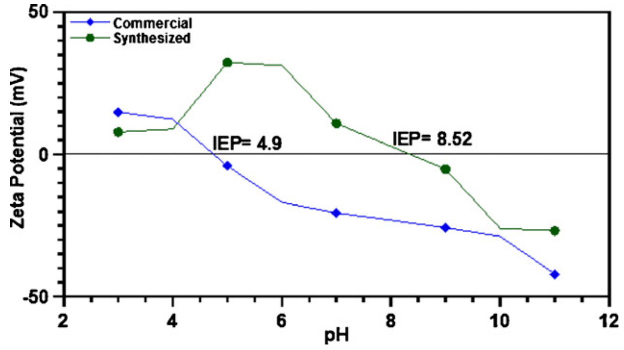

Fig. 2. Zeta potential of the commercial $CoAl_2O_4$ and the synthesised $CoAl_2O_4$ pigments as a function of pH.

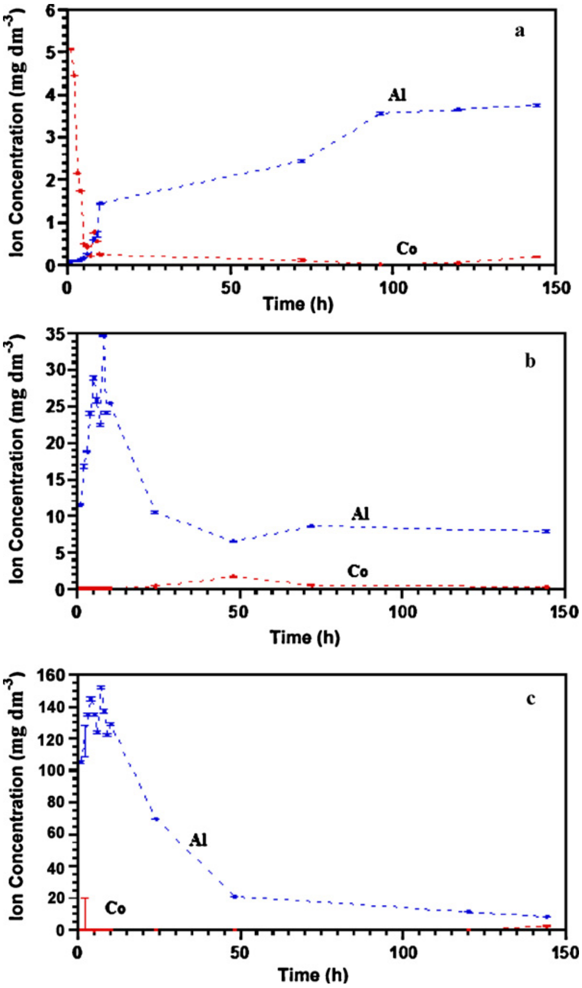

Fig. 3. Ion concentration of the synthesised $CoAl_2O_4$ pigment (500 nm) at (a) pH 7, (b) pH 9, and (c) pH 11.

Fig. 3 shows the ion concentrations of the synthesised $CoAl_2O_4$ pigment (500 nm) at different pH values (7, 9 and 11). The synthesised $CoAl_2O_4$ pigment system has no silicon ions in the aqueous suspension. The cobalt ion concentration was found to be similar for the three pH values. Therefore, it is concluded that cobalt ion is stable in the aqueous medium. However, the aluminium ion concentration changed as a function of pH. Aluminium concentration increased with increasing time at pH 7 and the total Al ion concentration reaches at plateau at 3.5 mg/dm^3 after 90 h. On the other hand, different dissolution behaviour was observed at higher pH values; it was initially (in 0–10 h interval) high, but it decreased from 30 mg dm^{-3} to 8 mg dm^{-3} at pH 9 and from 140 mg dm^{-3} to 10 mg dm^{-3} at pH 11 with increasing time.

Fig. 4 shows the particle size effect on the dissolution of the synthesised $CoAl_2O_4$ pigment at pH 9 for Al^{3+} and Co^{2+} ions. Although a very small cobalt ion concentration was observed in the suspensions, the aluminium ion concentrations for both 1 μm and 500 nm particle sizes decreased with time.

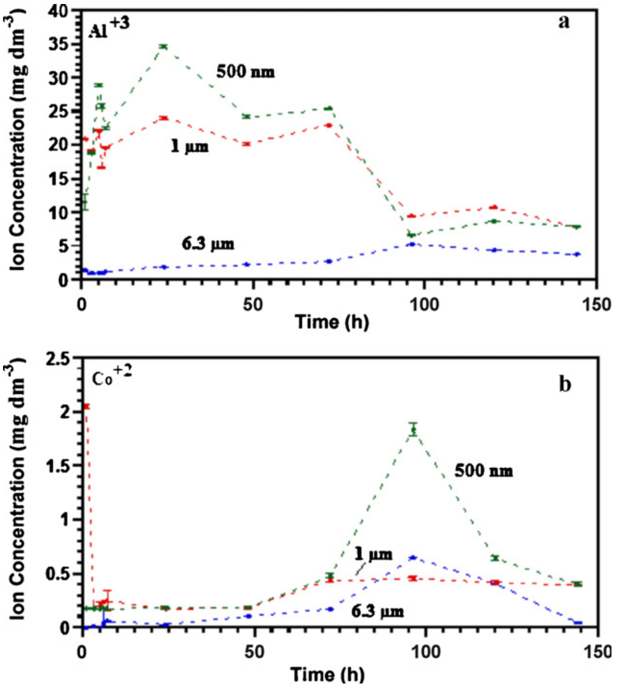

Fig. 4. Particle size effect on dissolution of the synthesised $CoAl_2O_4$ pigment at pH 9 for (a) Al^{3+}, (b) Co^{2+} ions.

Furthermore, measured concentrations were similar after 1 week (~10 mg dm^{-3}). These results suggest that a precipitation of a new phase may occur in a basic environment. Therefore, the received and aged pigment powders were examined by FT-IR analysis to test whether or not precipitation occurs in aqueous medium to clarify this phenomenon.

The infrared spectra of the received and dried pigment powders after treatment at pH 7, 9, and 11 for 20 days are shown in Fig. 5. The wave numbers of the main IR absorption peaks were observed at around 3445, 2858, 2930, and 1624 cm^{-1}. When α-Al_2O_3 (corundum phase) is found in commercial $CoAl_2O_4$ pigment powder, contact with moisture causes the powder surface to become hydrolysed. The O–H stretching vibration of Al-OH species that undergo hydrogen bonding with neighbouring hydroxyl groups in the corundum phase has been attributed as a broad peak at around 3445 cm^{-1}, and the shoulder at 1624 cm^{-1} arises due to the moisture in the sample. Absorption peaks at 2930 cm^{-1} and 2858 cm^{-1} show the existence of the $Al(OH)_3$ phase, which is formed as a precipitate [15–18]. The process of the precipitation can be described by the following reaction:

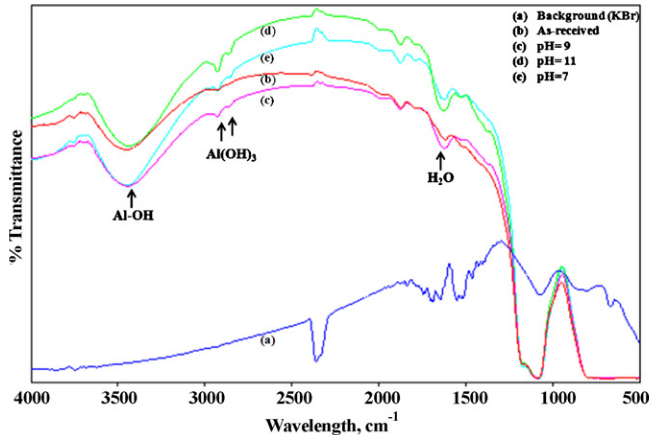

Fig. 5. FT-IR spectra of the as-received and the aged synthesised $CoAl_2O_4$ pigment as a function of pH.

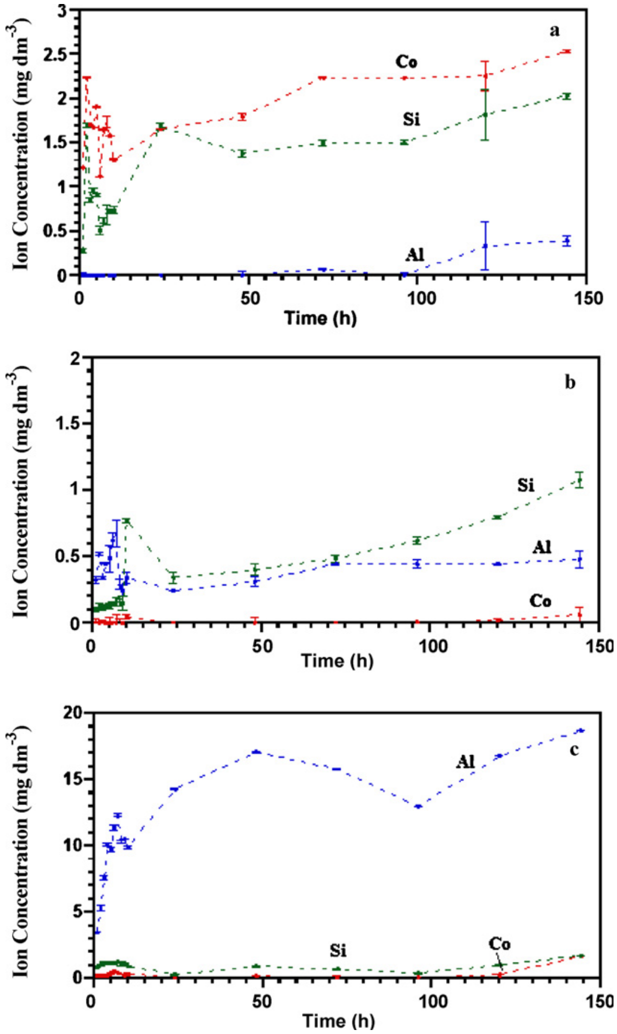

Fig. 6. Ion concentration of the commercial $CoAl_2O_4$ pigment (500 nm) at (a) pH 7, (b) pH 9, and (c) pH 11.

$$Al^{3+}(aq) + 3OH^{-}(aq) = Al(OH)_3(s) \qquad (2)$$

In FTIR spectra, $Al(OH)_3$ peaks were not observed in the as received pigment system except for peaks attributed to Al-OH species due to the hydrolysis of the corundum surface and H_2O as moisture. Consequently, $CoAl_2O_4$ pigments are affected by the aqueous medium and aluminium ions, and they dissolve from $CoAl_2O_4$ pigment and precipitate as $Al(OH)_3$ phase in pigment-water suspensions.

Fig. 6 shows the ion concentration variation of the commercial $CoAl_2O_4$ pigment (500 nm) as a function of time at different pH values in an aqueous medium. The total ion concentration of suspensions prepared with commercial $CoAl_2O_4$ pigment powder increases with increasing time when the pH increases to 11. The minimum ion concentration (<1.5 mg dm^{-3}) was obtained at the natural pH (pH 9) value (Fig. 6b). The ion concentration increases (>1.5 mg dm^{-3}) with the addition of acid at pH 7 (Fig. 6a). However, the degree of dissolution at pH 7 is lower than that at pH 11. In addition, the cobalt and silicon ion concentrations were stable in the solution at pH 11, whereas the aluminium ion concentration reached 20 mg dm^{-3} with increasing time (Fig. 6c).

The surface properties of alumina are affected by two main parameters: acidity and basicity. The dissolution behaviour of aluminium oxides strongly depends on the pH of the aqueous solution and typically increases at both acidic pH, below the pH of the IEP, and in the alkaline region. Surface atoms have incomplete bonds that can cause hydration to complete the coordination shell. Thus, surface hydroxyl groups are produced by the adsorption of H^+ ions on the oxygen sites and OH^- ions on the aluminium sites, which results in weakness of metal-oxygen lattice bonds and accelerates the detachment of ions. The dissolution phenomena of aluminium oxide in water are based on this interaction mechanism [19]. As a result, hydroxyl promoted dissolution and proton promoted dissolution are the main dissolution mechanisms of Al_2O_3 in basic and acidic media, respectively.

At pH 7 and pH 11, the silicon ion concentration in the commercial $CoAl_2O_4$ pigment (500 nm) system was found to be 2 mg dm^{-3} and 1.2 mg dm^{-3}, respectively (Fig. 6a and c). As reported in the literature, the dissolution rate of quartz is constant at neutral pH (typically 4–5). Above pH 5, hydroxyl-promoted dissolution becomes dominant and increases exponentially. Below pH 5, proton-promoted dissolution is dominant, and the dissolution rate increases exponentially with increasing hydrogen ion concentration [20,21].

Quartz in $CoAl_2O_4$ commercial pigments is not an essential additive to improve colouring yield of the production. However, both quartz and $CoAl_2O_4$ phases in the commercial pigment affect the dissolution behaviour of each other simultaneously. Therefore, dissolution behaviour of pure quartz in an aqueous medium was also investigated in this study. The aqueous suspensions which contain 5 wt% pure quartz powders were magnetically stirred in a polyethylene (PE) bottle for first 10 h, and ultrasonication was also used to achieve high dispersion of the particles. Ion concentrations of the suspensions at pH 7 (natural pH of quartz particle), 9 and 11 were determined as a function of time (Fig. 7). The ion concentration of pure quartz in the distilled water increased with increasing pH and reached high concentration levels of approximately 800 mg dm^{-3} at pH 11 as a function of time. As a result, in the commercial pigment system, pigment cations (in particular Al^{3+}) can be adsorbed onto the quartz surface, which can reduce the dissolution rate of quartz particles. In the literature, the stability of quartz particles in aqueous medium can be enhanced by Al^{3+} ions, as reported by Lortz et al. [22]. In addition, Bickmore and co-workers demonstrated that increasing the $Al(OH)_4^-$ ion concentration in the suspension suppresses the dissolution of quartz particles [23], which also explains why high Al^{3+} cation concentrations could not be observed even at the initial stage for the commercial $CoAl_2O_4$ pigment system. The dissolved Al^{3+} cations are probably absorbed on the quartz surface, resulting in low Al^{3+} ion concentrations in the suspension.

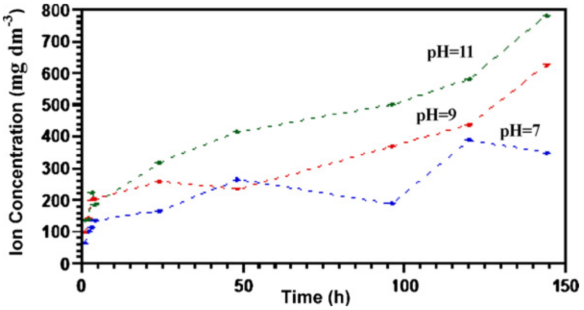

Fig. 7. Dissolution of pure quartz (99 wt%) powder having 1 µm particle size depends on pH.

The particle size effect on the dissolution behaviour of the commercial $CoAl_2O_4$ pigment (Fig. 8) showed that generally decreasing the particle size causes a small reduction in the dissolution of pigment cations. However, increasing the surface area of the pigment particles should create a high amount of dissolution. The reason may be proton adsorption on the negatively charged pigment surface or precipitation of some

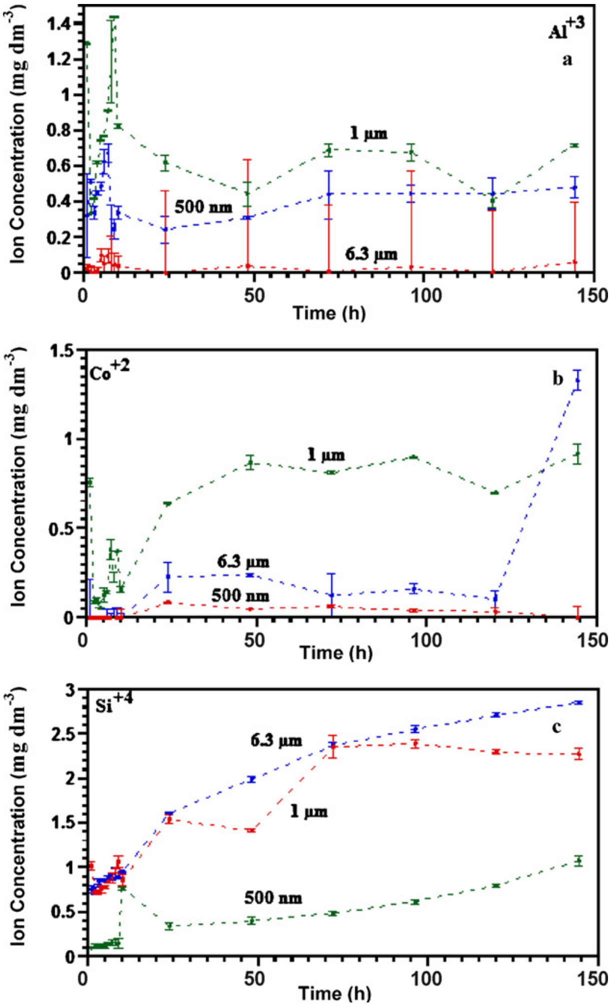

Fig. 8. Particle size effect on dissolution of the commercial $CoAl_2O_4$ pigment at pH 9 for (a) Al^{3+}, (b) Co^{2+} and (c) Si^{4+} ions.

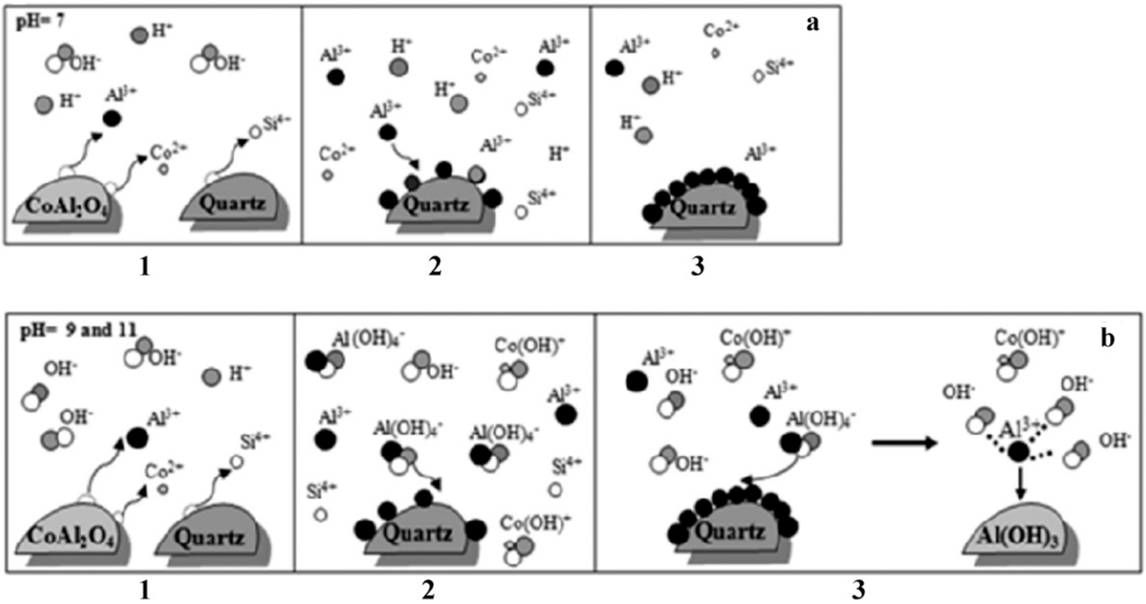

Fig. 9. Schematic showing the dissolution of pigment particle and the formation of the $Al(OH)_3$ precipitate (a) at pH 7: (1) Dissolution of pigment cations. (2) Transportation of the dissolved cations from the particle surface to the suspension. (3) Adsorption of Al^{3+} ions onto the quartz surface and (b) at pH 9 and 11: (1) Dissolution of pigment cations. (2) Transportation of the dissolved cations from the particle surface to the suspension. (3) Adsorption of Al^{3+} ions onto the quartz surface as $Al(OH)_4^-$.

cations as a new phases such as $Al(OH)_3$, which is shown by FTIR analysis.

In Fig. 9, a schematic showing the dissolution of a $CoAl_2O_4$ pigment particle and the formation of the $Al(OH)_3$ precipitate is given. The possible dissolution steps are summarised as

At pH 7

1. Dissolution of pigment cations.
2. Transportation of the dissolved cations from the particle surface to the suspension.
3. Adsorption of Al^{3+} ions onto the quartz surface.

At pH 9 and 11

1. Dissolution of pigment cations.
2. Transportation of the dissolved cations from the particle surface to the suspension.
3. Adsorption of Al^{3+} ions onto the quartz surface as $Al(OH)_4^-$, precipitation reaction of hydroxyl ions with pigment cations and formation of the $Al(OH)_3$ phase.

The dissolution process can be described in two stages: adsorption and desorption processes. The adsorption process includes two main steps. The first step is the transport of ions from the solution near the oxide particle surface. The second step is the attachment step, which results in the formation of bonds between the adsorbate and adsorbent where the critical oxygen-metal bonds polarise and weaken. Protons bonded to the oxide surface sites are mobile reactants, which means that surface protonation occurs randomly, and the protons may move from one functional surface site to another. Then the process of desorption becomes predominant, which also involves a two-step reaction: detachment and transport of ions. The detachment of the metal ions occurs after sufficient proton adsorption onto the metal centre of the oxide surface [24,25].

According to the results here and those reported in the literature, it is proposed that the $CoAl_2O_4$ blue pigments dissolve with proton promoted and hydroxyl promoted dissolution mechanisms in aqueous media. The existence of silicon ions from the quartz phase in the $CoAl_2O_4$ blue pigment affects the dissolution and chemical behaviour of Al^{3+} ions. In

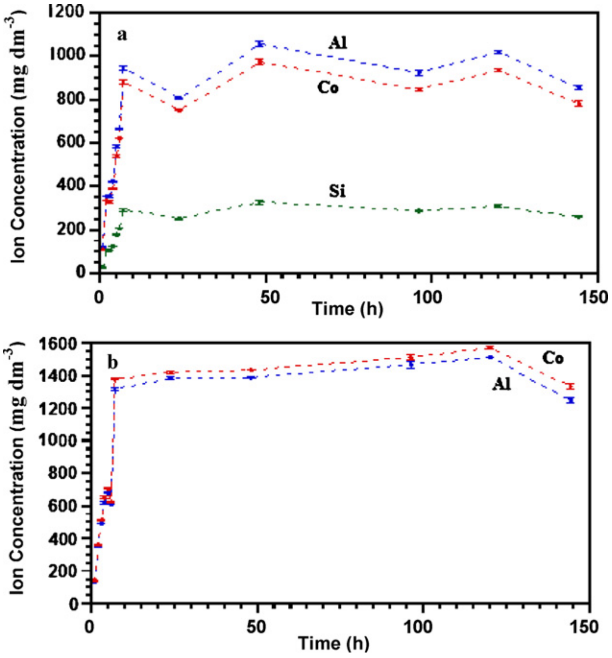

Fig. 10. Ion concentrations of (a) the commercial (b) the synthesised $CoAl_2O_4$ pigment in DEG medium.

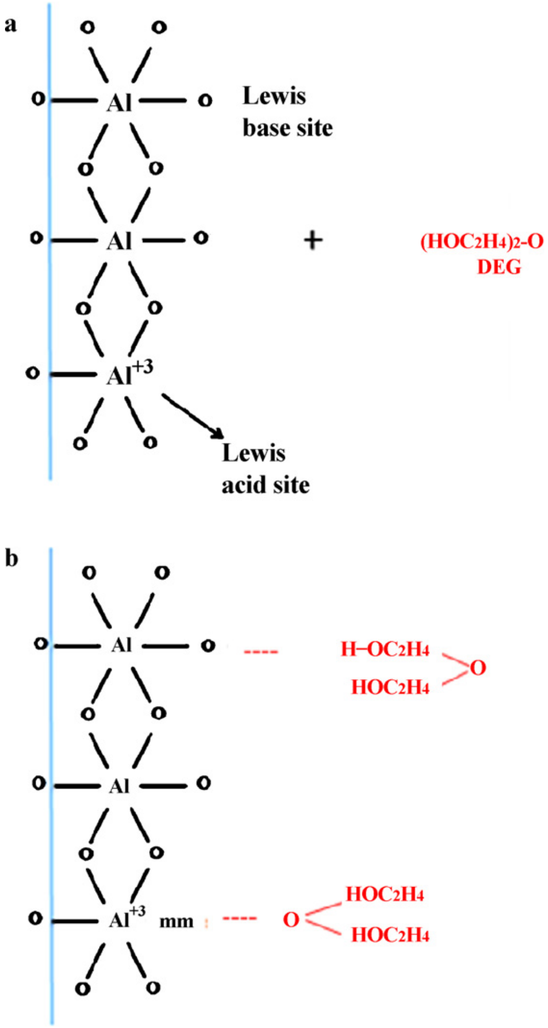

Fig. 11. Proposed dissolution mechanism of the Al_2O_3 surface in DEG medium: (a) surface groups and (b) interaction between surface and DEG and formation of surface complex which promotes cation dissolution: Lewis base site can interact with the DEG chain to form a surface complex while Lewis acid site can interact with the DEG chain to release Al^{3+} cations of the pigment particle into the suspension.

the synthesised pigment, Al^{3+} ions prefer to precipitate as $Al(OH)_3$ at basic pH values, whereas Al^{3+} ions in the commercial pigments favour adsorption onto the quartz surface as $Al(OH)_4^-$, which can also result in a reduction in the dissolution of quartz particles in basic media.

3.4. Suspension characterisation in non-aqueous medium

Fig. 10 shows the interaction between the pigment particles and the DEG medium. Both the commercial and the synthesised pigment powders exhibit increasing ion concentration with time in the non-aqueous medium. Aluminium and cobalt ion concentrations in the DEG medium exceed 800 mg dm^{-3} with increasing time. In addition, the silicon ion concentration in the non-aqueous medium reaches up to 300 mg dm^{-3}, which is lower than the aluminium and cobalt ion concentrations. As discussed above, the attachment and detachment steps first depend on the adsorption behaviour of ions onto the oxide surface.

Unfortunately, there is limited literature about $CoAl_2O_4$ dissolution in water and DEG medium. On the other hand, Al_2O_3 surface behaviour under various conditions has been reported [26–28]. According to this literature, Al_2O_3 can have two main surface groups as shown in Fig. 11a. Alumina surface is considered to have both Lewis acid (Al^{3+}) and base sites (Al–O) [29]. Based on Lewis theory, an acid is species that is an electron-pair acceptor while Lewis base is a species that is an electron-pair donor. The Lewis base site can interact with the DEG chain to form a surface complex while the Lewis acid site can interact with the DEG chain to release Al^{3+} cations of the pigment particle into the suspension as shown in Fig. 11b. This type of dissolution can be called as ligand promoted dissolution. The similar dissolution behaviour also expected for Co^{2+} cations. Accordingly, both Co^{2+} and Al^{3+} ion concentrations are much higher in DEG medium (Fig. 10) than those in water (Fig. 6). These results clearly show that the $CoAl_2O_4$ pigment has less chemical stability in diethylene glycol (DEG) medium with respect to aqueous suspensions.

4. Conclusions

In this study, the behaviour of the $CoAl_2O_4$ ceramic pigment in aqueous and non-aqueous media was investigated. The results can be summarised as follows.

- The cobalt ion concentration in distilled water remains low and constant, which indicates that the cobalt ion is stable in both the commercial and the synthesised pigment structure.
- The Al ion concentration in the commercial $CoAl_2O_4$ pigment–water system changes as a function of pH. However, the Al ion concentration in the synthesised $CoAl_2O_4$ pigment–water system decreases with increasing pH value as a consequence of the precipitation of Al ion as $Al(OH)_3$, which was confirmed by FTIR analysis in support of the chemical interaction between the pigment particles and distilled water, including HCl and NH_4OH solutions.
- According to the results here and in the literature, the $CoAl_2O_4$ blue pigments dissolve with proton promotion in acidic media, whereas the hydroxyl promoted dissolution mechanism occurs in basic aqueous media.
- In a non-aqueous environment, the dissolution of pigment particles is the highest. DEG chains probably form ligands with Al and Co ions as a Lewis acid–base coordination interaction on the oxide surface and enhance dissolution rates. These results show that the pigment particles in non-aqueous suspensions are not stable. Aluminium and cobalt ion concentrations in the non-aqueous medium increase with time as a consequence of the ligand promoted dissolution mechanism.

In practical applications, ceramic inks are generally dispersed in a non-aqueous (DEG) medium. These organic-based media are toxic. Moreover, the ion concentrations in non-aqueous media are higher than those in aqueous ones, and they increase with time. Accordingly, ceramic inks cannot be stored for a long time due to the dissolution of pigment cations into the non-aqueous medium. The deterioration of colour properties of $CoAl_2O_4$ pigment system is due to the dissolution of chromophore ions, which are the cobalt ions, from the pigment structure. Thus, a water-based medium can be used to provide more environmentally friendly and reliable inks. The results of this study can be utilised to develop the stabilisation strategies of the pigments in aqueous media.

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