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Effect of ion concentration on viscosity, electrical conductivity and deposit weight of doped nano alumina prepared by electrophoretic deposition Mostafa Milani¹, Seyed Mohammad Mirkazemi², Seyed Mohammad Zahraee^{1*}

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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Viscosity influenced by cation addition when I₂ concentration is in critical value.
- Viscosity is not a pH dependent parameter rather is the dopant concentration dependent.
- Smaller cations such as Mg⁺² have higher influence on conductivity of suspension.



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ABSTRACT

Viscosity, electrical conductivity and deposit weight were determined for Electrophoretic deposition (EPD) Mg^{2+} , Y^{3+} , La^{3+} and Ce^{4+} -doped alumina's ethanolic suspensions prepared at dopant concentration between 350 to 1350 ppm. The concentration of XCly (X, y were: Mg, 2; Y, 3; Ce, 3 and La, 3, respectively) the charging salt, is also found to be a critical factor to control the viscosity. It is shown that the deposit weight is influenced by precursor concentration, but not by conductivity, viscosity or the pH of the suspension. All two way concentration interactions without Mg²⁺ and Ce4+ concentration simultaneous change are significantly in analysis of variance (ANOVA) model. The viscosity of suspension reached 2.5 mPa.s with Mg²⁺, Y³⁺, La³⁺ and Ce⁴⁺ decreased to 100, 100, 100 and 0 ppm in low iodine concentration (400 ppm), due to the most heavily cations that can adsorb to alumina surface with iodine adsorption but lighter Mg²⁺ cations adsorb under the influence of OH groups excite on alumina surface. The interest in the present study is to achieve a model between viscosity and additive concentration.

1. Introduction

Electrophoretic deposition (EPD) is a colloidal shaping method for preparation of ceramic particle's deposits of overall thickness from nanometers to several millimeters [1]. EPD has the advantages of little training time, some restriction of the shape of the substrate, the ability to mass production and no requirement of binder burnout because of little or no organic matter. The EPD of ceramics was first studied by Hamaker in 1940 [2]. In all previous studies main task is the control of deposited mass onto electrode. Suspension characteristics, such as solid content, zeta potential, conductivity, viscosity, etc., are key parameters of the EPD mass controlling [3]. In Hamaker equation the deposition weight (w) during the EPD process can be described by:

$$w = fC\mu SEt$$
(1)

where C, μ , S and t are the particle concentration, electrophoretic mobility of particles, deposition area and deposition time, respectively; E is the electrical field (E = U/d), U and d are the applied potential and distance between the electrodes, respectively. There is general agreement that further work needs to be done to develop a full, quantitative understanding of the fundamental mechanisms of EPD to optimize the working parameters for a broader use of EPD in materials processing [4].

Suspension viscosity has an important role in various shaping methods such as slip casting [5-7], spry freeze drying [8] and EPD [9–11]. Stuer and Bowen [12] investigated the effects of different concentrations of dopants (Mg^{2+} , La^{3+} , Y^{3+}) on the aqueous suspension rheological behaviour of alpha alumina suspensions to achieve high solid loadings and low viscosity suspensions. Their results show that dopant addition increases the viscosity, and also causes a yield stress to appear. Upon their results, in higher cation charge at constant cationic concentration, higher effect on the double layer thickness and hence on the measured shear stress was observed [12]. Biswas et al. [13] studied the viscosity of lanthanum doped alumina suspensions. La₂O₂ used as precursor for lanthanum. When La₂O₃ weight increased suspension viscosity increased.

In EPD process The Henry equation relates the electrophoretic mobility to the viscosity.

$$\mu = \frac{\zeta \cdot \varepsilon_0 \cdot \varepsilon_{r,l}}{\eta} f(\frac{1}{\kappa}, a)$$
(2)

where, ζ (mV), is the zeta potential, $\varepsilon^{0}(8.8544 \times 10^{-12} \text{ A}^{2}\text{s}^{2}/\text{Nm}^{2})$, is the vacuum dielectric constant, εr ,l, is the solvent dielectric constant, η (Pa s) is the solvent viscosity and f(1/ κ , a), is a function of the particle radius, a (nm), and the Debye length, 1/ κ (nm). Depending on the viscosity of the solvent, suspensions with a similar dielectric constant and zeta potential shows large differences in the electrophoretic mobility of the particles. Given the Smoluchowski approach for thin double layer and large particles (a >> 1/ κ) powders with a similar zeta potential move faster in solvents with lower viscosities,

$$\mu = \frac{\zeta \varepsilon_0 \varepsilon_r}{\eta} \tag{3}$$

In all cases, dopant level are constant and relationship between concentration and viscosity are not investigated. Also, since the electrophoretic mobility and viscosity have close relevance dopant level can determine electrophoretic mobility and final deposition yield. The present work investigated the viscosity of ethanolic suspension of doped alumina nano powder to understanding electro-deposition behavior of this suspension. In this way, relation between dopant concentration, viscosity and electrophoretic mobility investigated and developed an equation for viscosity of suspension in present of cationic dopants. As a result, the cationic concentration in the suspension was optimized by means of viscosity measurements. Mg²⁺, Y³⁺, La³⁺ and Ce⁴⁺ used as dopant cations and 1/2 fraction, 2-level factorial design with 4 center points used for experimental design [14].

2. Experimental

2.1. Suspension preparation

Ethanol (Ph Eur, CAS 100986, purity 99.6 vol.%) without further purification is used as the dispersing medium. The dispersant used is iodine (I_2 , 99.8%) all were supplied by Merck Millipore, Germany. Specifications of the alumina nano powder was used presented in Table 1. Impurity analysis by the inductively coupled plasma atomic emission spectroscopy ICP–OES method was shown in Table 2.

Table 1.	
Characterization	of alumina powder

Supplier	Model	Purity (%)	BET surface area (m^2/g)	median particle size (nm)	Structure
US Nano, US	US3008	99+	19.95	80	corundum

Table 2.

Table 3.

Alpha alumina impurity determined by ICP-MS

Impurity	Mg	Κ	Ga	Na	Fe
Concentration (ppm)	411	20	40	10	10
	Y	Zn	La	Ce	Ca
	11	18	2	5	40

The amounts of magnesium oxide (MgO), yttrium (III) oxide (Y_2O_3), lanthanum (III) oxide (La_2O_3), and Cerium (IV) oxide (CeO₂) were varied as grain growth inhibitor to study their effects on viscosity and deposited weight of alumina nano powder. For all 20 different powders, the influence of the dopant concentration in constant potential and time were investigated according to an experimental matrix (Table 3). To dope the powder and prepare the suspensions for EPD, 50 g of alpha alumina nano powder was dispersed in 100 mL ultra-pure ethanol before addition of the desired amounts of a 400, 600 and 800 ppm iodine solution as

a dispersant. After an ultrasonic bath (UB) treatment of 15 min, Mg^{2+} , Y^{3+} , La^{3+} and Ce^{4+} ethanolic solutions (purity > 99.99%, Sigma Aldrich chloride salts) were added. The amounts of doping agent (cationic ratio [doping element^{X+}]/[Al³⁺]) introduced were 350 to 1350 ppm total cationic ratio. The final suspensions with an Operational pH (O.pH, pH in non-aqueous solvents) around 4 to 7 were stirred and UB treated for another 15 min before the electrophoretic deposition.

These different powders are referred to as I-Mg-Y-La-Ce as a XXXXX number, to indicate the cationic dopant as well as the dopant elements (Mg = magnesium, Y= yttrium, La = lanthanum and Ce = Cerium; all dopants were added in three concentration (Table 3) for all doping samples). After stirring and ultrasonication, the suspensions were loaded in a deposition cell.

StdOrder	RunOrder	Code	Iodine (I)	MgO(Mg)	$Y_{2}O_{3}(Y)$	La_2O_3 (La)	CeO_2 (Ce)
9	14	41110	400	100	150	100	0
13	7	41133	400	100	150	300	300
10	17	41413	400	100	450	100	300
14	20	41430	400	100	450	300	0
11	8	43113	400	300	150	100	300
15	19	43130	400	300	150	300	0
12	16	43410	400	300	450	100	0
17	10	623211	600	200	300	200	150
18	18	623212	600	200	300	200	150
19	5	623213	600	200	300	200	150
20	6	623214	600	200	300	200	150
1	15	81113	800	100	150	100	300
5	3	81130	800	100	150	300	0
2	4	81410	800	100	450	100	0
6	2	81433	800	100	450	300	300
3	9	83110	800	300	150	100	0
7	7	83133	800	300	150	300	300
4	12	83413	800	300	450	100	300
8	13	83430	800	300	450	300	0
16	1	83433	800	300	450	300	300

Experimental matrix (according to sample code order)

2.2. Deposition process

After suspension preparation, samples were deposited on a stainless steel electrode with a Ti_6Al_4V counter electrode (50 mm×40 mm×2 mm). Electrodes were cleaned with dipping in 1 M HNO₃ acid, rinsed with deionized water and acetone. Electrophoretic deposition was carried out in a polytetrafluoroethylene (PTFE) cubical cell of about $50 \times 40 \times 44$ mm³ and a capacity of 85 mL. The potential and distance between the electrodes is fixed at 50 V and 10 mm respectively. Electrodes were removed from the colloidal suspension, after 300 s of deposition processing, and were carefully removed and the deposits were left to dry at room temperature for 24 hours. These green bodies were easily removed from the electrode and were then weighed to determine the yield.

2.3. Characterization

Conductivity and pH of the suspension were measured at room temperature 10 min before and after the electrodes were immersed in the suspension. Conductivity was measured with a Cond 330i probe (WTW, Weilheim, Germany) and pH was measured with a pH meter (Mi180, Milwaukee, Szeged, Hungary) at room temperature $(25.0 \,^\circ\text{C} \pm 0.5 \,^\circ\text{C})$. Three aqueous standards of pH 4, 7 and 10 were used for calibration due to the lack of standard buffer solutions for ethanol. Thus, the pH meter determines so-called "operational pH values" (O.pH) for nonaqueous suspensions. The theoretical background and method involving O.pH was described by Wang et al. [15]. The viscosity of suspensions was measured with a viscosity meter (type DV2T Viscometer, Brookfield, USA) that equipped by small sample adapter (SSA). During the rheology measurements, the setup and the suspensions were kept at 25 ± 0.1 °C by a thermostatic bath. The data acquisition cycle was: (1) ramp from 0 to $180 \,\mathrm{s}^{-1}$ in 30 s, (2) hold at $180 \,\mathrm{s}^{-1}$ for 60 s, and (3) decrease from 180 to 0 s^{-1} in 30 s. The data acquisition was performed three times on the same suspension with the same cycle with 1 min waiting time between the cycles.

2.4. Method

The viscosity and deposited weight results were analyzed by statistical analysis of variance (factorial ANOVA) [14]: by conducting different series of independent experiments, and combined into one matrix, the effect of the interacting parameters to be considered as well as giving the statistical significance of variations of properties as a function of the different experimental parameters. The effect of the parameters, cation concentration, iodine concentration, and possible interactions between them on the measured property (i.e. viscosity or deposited weight) are determined within a confidence interval of 95% ($p \le alpha$ level) according to standard statistical analysis [14].

3. Results and discussion

3.1. Stability of suspension

Stability of suspension characterized by sedimentation time of half of powder in suspension. In all suspensions more than 180 min were required to sediment half of added powder. On the other hand in lower viscosity the sedimentation time increased and exceeded to 300 min.

3.2. Cation adsorption mechanism

Figure 1 presented conductivity measurement of alumina/iodine suspensions by adding cations from 0 to 4000 ppm separately. From all suspension parameters, pH and conductivity of the suspension could be measured as a macroscopic result to understand the cation adsorption mechanism. To understand the adsorption mechanism of cations in surface of particles in suspension, the conductivity of suspension with and without alumina addition were measured. Ethanol conductivity measurement by addition of cations indicated in Figure 2. As can be seen, for all cations the conductivity of suspension and ethanol increases with increasing of the doping concentration of cations. The increase in conductivity with cation addition at present of iodine can be explained by the following reactions:

$$CH_3 - CH_2 - CH_2 - OH + I_2 \rightarrow CH_3 - CH_2 - CHO + 2HI \quad (4)$$

$$MCl_{x} + xHI \xrightarrow{l_{2}} M^{+x} + xHCl + xI^{-}$$
(5)

The increment of the conductivity as a result of iodine addition and cations addition into the ethanol is due to the generation of ionic species (CI, I, M^{+x} and H⁺) in them. When alumina was adds to ethanol these ions released in the process can adsorb to alumina surface and formed electrostatic forces between particles created a stable suspension [16]. Decrement in electrical conductivity after addition of alumina in same cationic concentration (difference between Figure 1 and Figure 2) can be mainly attributed to the adsorption of ions on alumina surfaces which cannot contribute to electrical conductivity of suspension. When ethanol molecules were adsorbed on nano alumina surface powder OH and CH, groups creates a positive charge on this surface [17,18] and the Iodine and Chlorine anion were adsorbed firstly on the surface of the suspended particles making them negatively charged. Then heavily cations electrostatically adsorbed to this anions. As a result this charged particles and some portion of non-adsorbed ions increased the conductivity of suspension by increasing of cation concentrations in same iodine concentration.

In competition, a drastic increase of conductivity is obtained by increasing Mg^{2+} concentration, while no significant difference of conductivity values is found when increasing Y^{3+} , La^{3+} and Ce^{4+} , concentrations from 0 to 4000 ppm, indicating that the increase of conductivity is mainly influenced by the addition of Mg^{2+} .

According to this results if the concentration of I ions is lower than the critical concentration there will be numerous free ions with high ability to move. It causes higher conductivity of suspension. When this concentration reaches to a critical value all of the alumina particles will be surrounded by all cations. The formed charged particles are bigger than free ions and could not participate in current transition, it results in low suspension electrical conductivity. The schematic of the formed species with different iodine concentration is illustrated in Figure 3. Iodine and Chlorine anions adsorbed to alumina surface. These large anions can adsorb cations. When iodine concentration equals to critical concentration the coating of cations have the most uniformity (Figure 3b). Figure 3a and c are showing the adsorption morphology in which iodine concentration is lower and higher than the critical value, respectively.

This mechanism resulted the negative charged suspended alumina particles and promote the anodic deposition. On the other hand, the pH in all suspensions was approximately 5.8 ± 1.5 , which is below the alumina IEP (isoelectric point) in ethanol [19] indicating that the particles were negatively charged in presence of iodine and proved anodic deposition. Another proof of the adsorption of cations on the surface of the suspended particles is discussed in below by chemical analysis results.



Fig. 1. Conductivity changes of suspension by separated cation concentration. Suspension made by 100mL ethanol, 400 ppm Iodine and 20 g alumina nano powder. Lanthanum concentration (\blacklozenge), Yttrium concentration (\blacksquare), Cerium concentration (\blacktriangle) and Magnesium concentration (\blacklozenge).



Fig. 2. Conductivity of ethanol by adding cations separately. Lanthanum concentration (\bullet) , Yttrium concentration (\bullet) , Cerium concentration (\bullet) .



Fig. 3. A schematic representation of the alumina surface in ethanol in present of iodine anions and solved cation salts. Iodine concentration a) < critical concentration, b) = critical concentration and c) > critical concentration.

3.3.ANOVA Analysis

In the earlier work, we found that charged nano alumina particles by positively ions reached toward the electrode successfully [20]. In this investigation the EPD of nano alpha alumina using two level factorial design has been studied. The properties of the suspensions that were prepared with various conditions are summarized in Table 4. Design consisting of 4 center points and 16 axial points that rendered a total of 20 runs of experiment. In this study, the response variables measured were deposit weight (g) and viscosity (mPa.s), pH and conductivity (uS/cm) of suspension. All suspensions were stable in 3 h after preparation and no sedimentation occurred during this time. Low viscosity of the suspensions confirm this stability. Two level factorial design is considered as a useful method when the response is influenced by several variables. In addition to a useful mathematical and statistical technique for modeling and assessment of effects of factors at different levels and interactions between factors. This technique is applied in an experimental model to provide mathematical and statistical technique for modeling and analysis of engineering problems.

The viscosities of the suspensions were increased from 2.50 mPa.s to 6.10 mPa.s at shear rate of 120 s^{-1} (Table 4) and these increase were not associated with the increasing or decreasing of ionic concentrations. Figure 4 shows half normal probability plot of viscosity. Since the signs of the estimated effects are arbitrary, there are recommended the use of the half-normal probability plot of effects over the normal probability plot. In half normal plots the estimated effect of a factor is generally unimportant on or near a line close to zero, while the estimated effect of an important factor will generally move well out of line. According to Figure 4, all two interaction parameters have significant effect on viscosity without interaction between Mg²⁺ and Ce⁴⁺ concentrations. All primary factors except Mg²⁺ concentration categorized in not significant effects. Mg²⁺ has lower cationic radius and adsorb on surface of nano alumina powders and produce a high repulsive energy between them, but other cations with higher cationic radius have lower charge density and lower repulsive energy.

Figure 5 shows the Pareto plot for viscosity.

Code	pН	Conductivity (µS/cm)	Deposit weight (g)	Viscosity (mPa.s)
41110	5.70	3.9	4.40	2.50
41133	5.66	5.4	4.00	5.98
41413	7.32	4.6	4.11	2.90
41430	6.42	3.9	5.76	3.05
43113	6.35	14.9	4.15	3.92
43130	6.13	6.5	5.26	3.32
43410	5.11	12.5	4.60	3.12
623211	6.14	5.5	3.65	5.42
623212	6.10	5.5	3.87	6.04
623213	5.90	5.2	3.45	5.87
623214	6.18	5.1	3.49	6.10
81113	5.04	6.0	3.39	2.52
81130	5.69	7.5	3.72	3.70
81410	6.12	10.7	3.06	2.90
81433	5.70	7.5	3.26	3.50
83110	5.27	13.2	4.72	3.37
83133	5.77	15.2	4.32	2.87
83413	4.60	15.1	4.20	3.15
83430	5.30	19.0	4.15	3.25
83433	4.80	10.6	4.13	3.35

 Table 4.

 Experimental results (according to sample code order)



Fig. 4. Half normal plot of the standardized effects for viscosity, $\alpha = 0.05$.

Pareto plot displays the absolute value of the effects and draws a reference line on the chart (3.182 in Figure 5). Any effect that goes beyond the reference line is potentially important. As before all two interaction factors except Mg × Ce and none of primary factors except Mg²⁺ concentration have significant effect. This result confirmed from the nonlinear 2D contour plots. Figure 6 shows a graph with graduated colors, hard blue for lower desirability and green for higher one. These 2D contour plots highlight the effect of additives concentrations on viscosity. It is clear that at higher iodine concentration, cation concentration played a major role in increasing the viscosity for Mg²⁺, Y³⁺ and La³⁺ cations. In the case of Ce⁴⁺ at high iodine concentrations, viscosity cannot be influenced by Ce4+ concentration. In low iodine concentration viscosity decrease in low Mg²⁺ concentration and high Y³⁺, La³⁺ and Ce⁴⁺ concentration. This is well in agreement with the mechanism will be discussed. When iodine concentration is higher than that of critical concentration viscosity increased by increasing in Y³⁺ and La³⁺ cations concentrations but decreasing in Mg²⁺ cation concentration. When Y³⁺ and La³⁺ cations that are larger cations add to suspension further iodine and these cations electrostatically adsorb on each other and increase viscosity. Cationic charge density can be explained this behaviour.

In iodine concentration lower than the critical concentration the surface of alumina nano powders cannot be completely covered by ions and enough repulsive forces cannot be produced to make stable suspension and reduce viscosity. Electrical conductivity of suspension confirm this mechanism.

Since the response function is linear, the linear model is employed. Equation 1 demonstrates the mathematical expression of the model.

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} \sum_{j=1}^{k} b_{ij} X_i X_j + e$$
⁽⁶⁾

where "i" and "j" determines the linear coefficients "b" is the regression coefficient, "k" is the number of experimental factors, and "e" is the random error.

The stability of the regression model is also estimated by an analysis of variance (ANOVA). The results shown in Table 5. In the first step, the probability of significance is determined. The effect of the independent variable is significant if the probability of significance (p) value is equal to or less than the selected alpha-level (here 0.05), and the insignificant variables are those with p values greater than the selected α -level [14].According to these, all two way interactions with the p value < 0.05 are significant except Mg²⁺ × Ce⁴⁺ cations concentrations with p value = 0.15. The model p value of 0.023 reveals that the model is still significant.

According to ANOVA model all interactions between iodine and cations i.e. $I \times M^{x+}$ are significant and showed that critical concentration of iodine is necessary to adsorb cations on alumina nano powder surface and reduced viscosity by repulsive electrostatic forces.

The final improved empirical models in terms of actual factors for viscosity is given in Eq. 7. Coefficients of individual factors and their interactions in the regression model shows how the response changes with respect to the interception.

Viscosity = 3.155 + 0.1331 I + 0.1419 Y - 0.2106 Mg - (7) 0.0244 La - 0.1194 Ce + 0.2831 I×Y -0.3019 I×Mg + 0.1994 I×La + 0.1719 I×Ce -0.2681 Y×Mg + 0.2956 Y×La + 0.2181 Y×Ce - 0.1894 Mg×La -0.0994 Mg×Ce + 0.1894 La×Ce - 0.267 I×Y×Mg×La×Ce

The model summary statistics for viscosity (mPa.s) are given in Table 6. The value of R^2 is 98.76%, which is very close to 1. Likewise, the adjusted R^2 value are in close agreement.

Relation between viscosity and additive cations concentrations showed by Matrix plot in Figure 7. It is obvious that all sections have semi linear profile and indicates that by increasing the concentration span in this EPD process, the viscosity decreased, although the effect of the La³⁺ and Ce³⁺ cations concentrations are more significant than that of the Iodine, Mg²⁺ or Y³⁺ cations concentrations. Figure 7 also showed curvilinear relation between additive concentration and deposited weight. Maximum deposited weight with a simultaneous relatively minimum viscosity is considered as desirable conditions. The optimal setting suggests that these outcomes can be achieved by varying the all concentrations to zero level. Deposit weight had a lower, average and upper value of 3.06, 4.08 and 6.04 g respectively (Table 4). If the values of deposit weight are divided in to 3 range, half of samples had weight between 4.06 to 5.06 g. Analysis indicated that the 5-way interaction have a higher effect on the deposition weight but is not a significant parameter (Figure 8a). According to Hamaker model deposit weight had direct relationship with electrophoretic mobility that increased when viscosity decreased or zeta potential increased [2]. Although deposition weight increased with a decrease in viscosity, there are not a linear relation between them, considering in some cases zeta potential increased although viscosity increased.



Fig. 5.Pareto plat of the standardized effects for Viscosity, $\alpha = 0.05$.



Fig. 6 . Contour plot of viscosity.

Source	Degree of freedom	Adj SS	Adj MS	F-Value	P-Value
Model	16	10.2456	0.64035	14.97	0.023
Linear	5	1.5529	0.31059	7.26	0.067
Ι	1	0.2836	0.28356	6.63	0.082
Y	1	0.3221	0.32206	7.53	0.071
Mg	1	0.7098	0.70981	16.6	0.027
La	1	0.0095	0.00951	0.22	0.669
Ce	1	0.228	0.22801	5.33	0.104
2-Way Interactions	10	8.4647	0.84647	19.79	0.016
I×Y	1	1.2826	1.28256	29.99	0.012
I×Mg	1	1.4581	1.45806	34.09	0.01
I×La	1	0.636	0.63601	14.87	0.031
I×Ce	1	0.4727	0.47266	11.05	0.045
Y×Mg	1	1.1503	1.15026	26.9	0.014
Y×La	1	1.3983	1.39831	32.7	0.011
Y×Ce	1	0.7613	0.76126	17.8	0.024
Mg×La	1	0.5738	0.57381	13.42	0.035
Mg×Ce	1	0.158	0.15801	3.69	0.15
La×Ce	1	0.5738	0.57381	13.42	0.035
5-Way Interactions	1	0.2279	0.22791	5.33	0.104
I×Y×Mg×La×Ce	1	0.2279	0.22791	5.33	0.104
Error	3	0.1283	0.04277		
Total	19	10.3739			

Table 5.Analysis of Variance for viscosity model

Table 6.Viscosity model summery

S	R-sq	R-sq(adj)	R-sq(pred)
0.206801	98.76%	92.17%	*



Fig. 7. Matrix plots of viscosity (mPa.s) and deposition weight (g) vs. additive concentrations (ppm).

According to observations of these research 2-way interaction between Mg2+ and Y3+ cations concentrations have significant effect on pH of suspension (Figure 8b). After that 5-way interaction have most effect (not-significant). pH of suspensions according to additive concentrations showed in Figure 9. pH changes have not a significant trend. On the other hand according to Figure 9 conductivity increased by increasing in I, Mg²⁺ and Y³⁺ cations concentrations. La³⁺ and Ce³⁺ cations concentrations have not significant effect. To summarize results between viscosity, deposited weight, pH and conductivity, Figure 10 exhibited Matrix plots of there. It seems deposit weight has been influenced by pH and conductivity although there are not a clearly relationship. Maximum deposited weight can be achieved in pH around 6 and electrical conductivity around 5 µS/cm. There is an important note that the yield obtained from the different suspensions with equal iodine/nano powder ratio can be attributed to what cations (Mg²⁺, Y³⁺, La³⁺ and Ce³⁺ cations concentrations in this work) change electrical conductivities and pH of the suspensions as a result of the different concentrations of added cation salts in the suspensions rather than to the different in amount of conductivities and pH values of the suspensions.

The pH in all suspensions was approximately $5.8 \pm$ 1.5, which was below the all reported for alumina IEP in ethanol [15,21,19], indicating that the particles were positively charged [20]. The dissociation of iodine resulted the negative ions, which then would reverse the charge of the suspended alumina nano powder and promote the anodic deposition. The effect of additive concentration on electrical conductivity of suspension were also investigated from the developed mathematical model. Figure 8c show Pareto plots of these model. According to Figure 8c Mg²⁺ cation concentration has significant effect on the electrical conductivity. Consequently, the ionic load increased with the increasing concentration of additives. The higher concentration of additives in the suspension implied a higher fraction of ions and thus there expected the suspension possessed a lower pH (for Cl⁻) and higher electrical conductivity. But it is not a linear relation between that. The experimental values obtained from ICP measurement were in good agreement with the calculated values in preparation step of the suspensions and No Fe, Cr or Ti and V (arising from the substrate or counter electrode) was detected in the deposited layer.



Fig. 8. Pareto plat of the standardized effects for deposition weight (a), pH (b), conductivity (c). $\alpha = 0.05$.



Fig. 9. Matrix plots of conductivity (μ S.cm⁻¹) and pH vs. additive concentrations (ppm).



Fig. 10. Matrix plots of deposition weight (g) and viscosity (mPa.s) vs. pH and conductivity (µS.cm⁻¹).

4. Conclusions

This work described the preparation of homogeneous doped alumina nano powder ethanol-based suspensions using the cation salts additives and iodine. It was confirmed experimentally that the additive concentration is an important key parameter that has an effect on the viscosity of the suspension. According to this work the lower viscosity of the suspensions in addition to cation salts might be expected in optimum concentration which may enable the particles to arrange themselves at more optimized positions in suspension by electrostatic forces. This mechanism could be represented for higher deposited weight. When viscosity decreased, optimized suspension lead to higher electrophoretic mobility and simultaneously deposited weight.

Based on the discussion of electrical conductivity, viscosity and pH value distributions during EPD, at the initial stage of EPD, charged particles move toward anode by electrophoretic motion and M^{+x} ions that must be move toward a cathode deposited with them in anode.

Conductivity increased by increasing in I, Mg^{2+} and Y^{3+} cations concentrations. La³⁺ and Ce³⁺ cations concentrations have not significant effect and Mg^{2+} cation concentration has significant effect on the electrical conductivity. Maximum deposited weight can be achieved in pH around 6 and electrical conductivity around 5 µS/cm.

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