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Effect of citrate, tartrate and gluconate ions on the behaviour of zinc in 3 M NaOH

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Abstract

Citrate, tartrate and gluconate are examined for their influence as additives to 3 M NaOH electrolyte for use with zinc. Solubility, turbidity and conductivity measurements are presented. Electrochemical oxidation and redeposition of zinc in the medium is investigated using cyclic voltammetry. Products of electrochemical reaction are analysed by IR and Raman spectroscopy. Tartrate and gluconate appear to produce micelles in the zincate medium whereas citrate appears to stabilize a polymeric structure in solution. Hull cell patterns of electroplating of zinc from zincate in presence of additives and morphology of the coatings by SEM pictures are also discussed.

Keywords: Zinc; Additives; Electrolyte

1. Introduction

Gagnon [1] showed that cells containing zinc electrode had less shape change, better capacity retention and longer cycle life when tested with 20 wt.% or 10 wt.% KOH in presence of calcium zincate as an additive. Some studies have also shown that when certain additives like calcium citrate [2] and calcium gluconate [3] are added to zinc electrode, the capacity retention and cycle life of Zn/NiOOH cells are improved. The chief influence [4–8] of calcium zincate has been to reduce the solubility of Zn/ZnO in the alkaline electrolyte. In order to understand the influence of other additives on the behaviour of zinc electrode in alkaline solutions, we carried out solubility, turbidimetry and cyclic voltammetry of zinc oxide/zinc as well as electrodeposition of zinc in NaOH media in the presence of citrate, tartrate and gluconate. The results are discussed in the light of spectral measurements.

2. Experimental

All solutions were prepared in twice-distilled water. Sodium citrate, potassium sodium tartrate and calcium gluconate were from E-Merck. ZnO (99%), a Qualigen chemical, was heat-treated at 973 K for 8 h before use.

2.1. Zincate preparation

Unless otherwise specified, the following zincate composition was used for all studies. ZnO: 12.6 g l^{-1}; sodium hydroxide: 120 g l^{-1}; pH: 12.6. The required quantity of zinc oxide was made in the form of a slurry with a minimum quantity of water. Then, required amount of NaOH was added with continuous stirring. The solution was filtered and made up to the required volume.

2.2. Solubility, turbidity and conductance measurements

Solubility measurement was made in the following way: ZnO was added to the electrolyte in small instalments and under constant stirring. When the first speck of undissolved species was noticed, the solution was filtered through a previously weighed crucible and the weight of zinc oxide was obtained. Turbidimetry was carried out

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using a Systronics (India) turbidity meter and the colour with naked eye. A Nucleonix (India) pH meter was used in the pH measurement.

2.3. Electrodeposition of zinc

A 267-ml Hull cell was used for studying the effect of additives on the deposit characteristics at various current densities. Mild steel specimens were mechanically polished, solvent degreased and alkali cleaned. Cell current passed was 1 A and the experiment was carried out for 5 min. SEM measurements were made on a Leica Cambridge Stereoscan 440 instrument. The specimen (after the completion of zinc plating) was washed repeatedly in distilled water, rinsed successively with methanol and acetone and then dried in vacuum. The specimens were stored under nitrogen before mounting in the scanning electron microscope.

2.4. Spectral measurements

The equipment for Raman spectra consisted of an argon ion laser and Jarrel-Ash 1 m double monochromator followed by a photon counting assembly. The samples were filtered through a G4 sinter before they were placed in the cell (1 cm quartz) for measurement. After each run, the cuvette was cleaned by immersion in concentrated HCl followed by a thorough washing with distilled water. Before each measurement the absence of carbonate was ensured by running the spectra for the band at 1065 cm^{-1} characteristic of carbonate. IR spectra were recorded on a Shimadzu 408 spectrophotometer using KBr cells.

2.5. Cyclic voltammetric measurement

Cyclic voltammetric studies were conducted using a home-made single compartment cell (0.01 m diameter) with a fused in platinum foil of large area (0.02 m × 0.04 m) as counter electrode. The working electrode was a pure zinc metal (99.9%) rod (2×10^{-5} m^2 area) embedded in a teflon mount. This electrode was polished with emery paper (4-0 grade), degreased with acetone and finally washed with triple distilled water. The experimental solutions were deaerated by passing oxygen-free nitrogen through them. The measurements were made at 25 ± 2°C using a BAS 100A electrochemical analyzer. Cyclic voltammograms of pasted zinc electrode (as a working electrode) were also registered under the same experimental conditions. The pasted zinc electrode material was made by compacting finely ground zinc oxide (with or without additive) mixed with a drop of binder on either side of a silver expanded mesh using a die and a hydraulic press. A compaction pressure of 3 tonnes was used. The specifications of the zinc paste electrode were as follows. Content: 0.3 g; dimension: 0.01 m × 0.01 m × 0.0005 m.

2.6. Isolation of products

In order to isolate and analyze the products formed during the anodic dissolution of zinc in 3 M NaOH in the presence of additives, we carried out constant potential macrodissolution of zinc in zincate (3 M NaOH). A zinc sheet (99.9% purity) of dimensions 0.02 m × 0.025 m × 0.03 m was used for this purpose and the solution (100 ml) was deaerated before commencing the dissolution; during zinc dissolution, the solution was continuously stirred on a magnetic stirrer while nitrogen was slowly bubbled at a slow rate. The dissolution was terminated at 0.5 h and the solution was cooled at 278 K and then it was allowed to stand at ambient temperature until the solution reached around 293 K. The solution was filtered on a G4 sinter at this temperature. The solid residue was first washed few times with 5% NaOH followed by repeated washing with distilled water and then dried in vacuum. This procedure of zinc dissolution and isolation of products was repeated until sufficient quantity of the product was collected.

3. Results and discussion

3.1. Solubility and conductance measurements

pH measurements (Fig. 1) have indicated that pH of zincate (3 M NaOH), which is around 12.6, is not altered significantly in the presence of the additives. In fact, there was a slight increase in the pH towards 13. In other words, high alkalinity necessary for battery performance is maintained by the additive. There is a reduction in the solubility of zinc oxide in the presence of additives (Fig. 2) and the decrease follows the order, gluconate > tartrate > citrate.

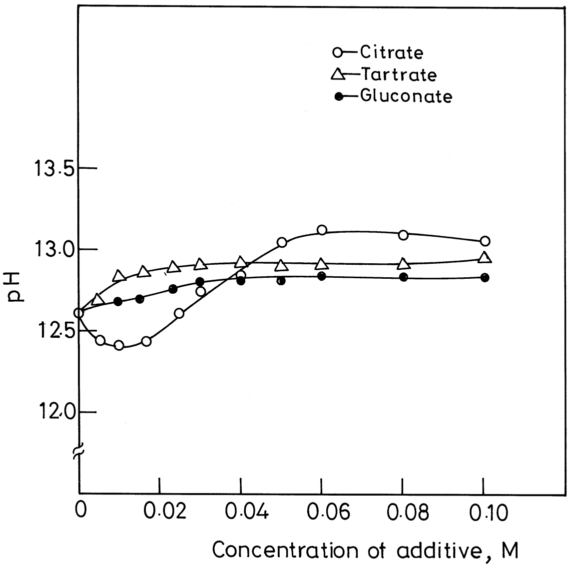

Fig. 1. Dependence of pH of zincate (3 M NaOH) on the concentration of the additive.

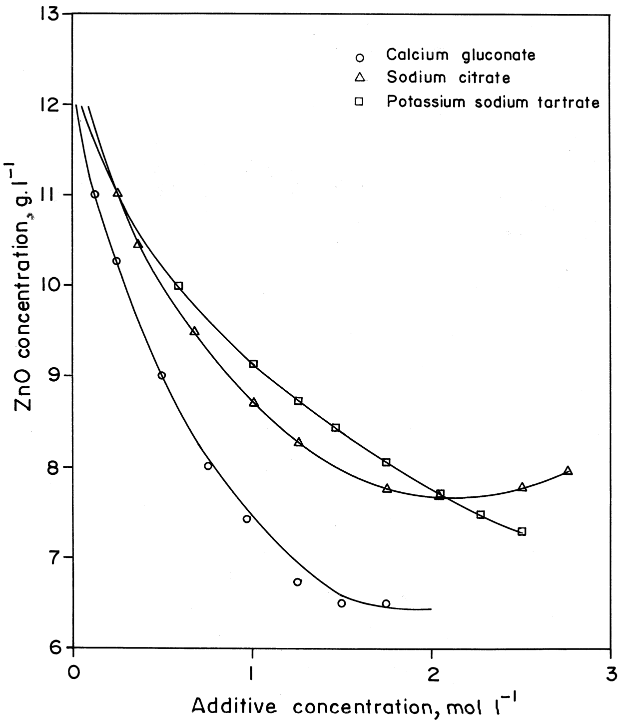

Fig. 2. Solubility of zinc oxide in 3 M NaOH in the presence of additives.

Fig. 3 shows the solubility pattern of ZnO in various concentrations of KOH in presence of the same additives. A comparison of Fig. 2 and Fig. 3 indicates that the trend in the effect of calcium gluconate on ZnO solubility in NaOH is similar to that of calcium gluconate on ZnO solubility in KOH. The comparison with KOH is of significance because it is the practical battery electrolyte.

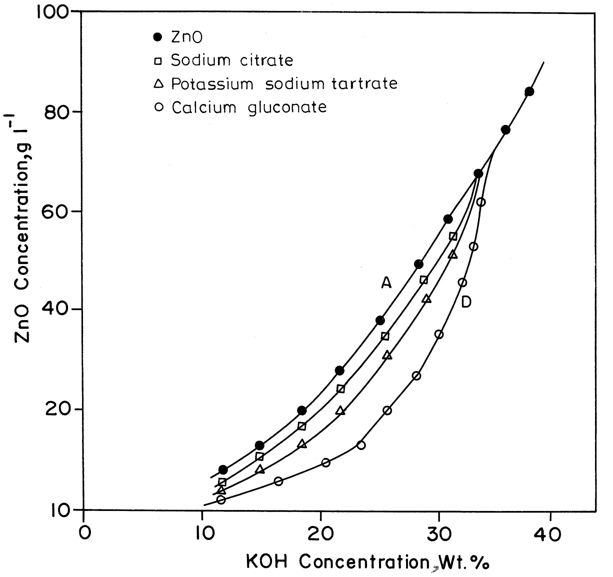

Fig. 3. ZnO concentration in KOH solutions at 303 K in the presence of additives (A) pure ZnO, (B) sodium citrate, (C) sodium potassium tartrate, and (D) calcium gluconate.

The specific conductance of zincate (3 M NaOH) is markedly influenced by the presence of additives in the solution. The specific conductance of zincate solution is 0.15 S cm^{-1} and the change produced in the conductance values are presented in Fig. 4. It can be seen that the additives each bring about a decrease in the conductance; the decrease escalates as the concentration increases. In the case of citrate, there is an initial decrease which eventually reaches a constant steady value above 2×10^{-2} M. In the case of tartrate and gluconate, the conductivity declines and then increases. The minimum point is around 1×10^{-2} M for tartrate and 2×10^{-3} M for gluconate.

The decrease in conductivity suggests a decrease in the quantity of conducting species in solution. The occurrence of a minimum point is suggestive of a micelle-like aggregation of the conducting species in solution because micellar aggregation is a concentration dependent process. A plot of a colligative property such as viscosity, light scattering intensity, osmotic pressure, conductance, etc. vs. concentration generally produces an inflection point at the critical micellar concentration (CMC) [9,10]. Turbidity measurements (Fig. 5) are also supportive of aggregation/micellization process because the particle size shifts from lower to higher value in the concentration range corresponding to the minimum point. In Fig. 6, curve a shows the IR spectrum of the compound obtained by constant potential macrodissolution of zinc in gluconate added NaOH solution. It can be seen that the OH bending modes which produce absorption peaks around 1450 cm^{-1}

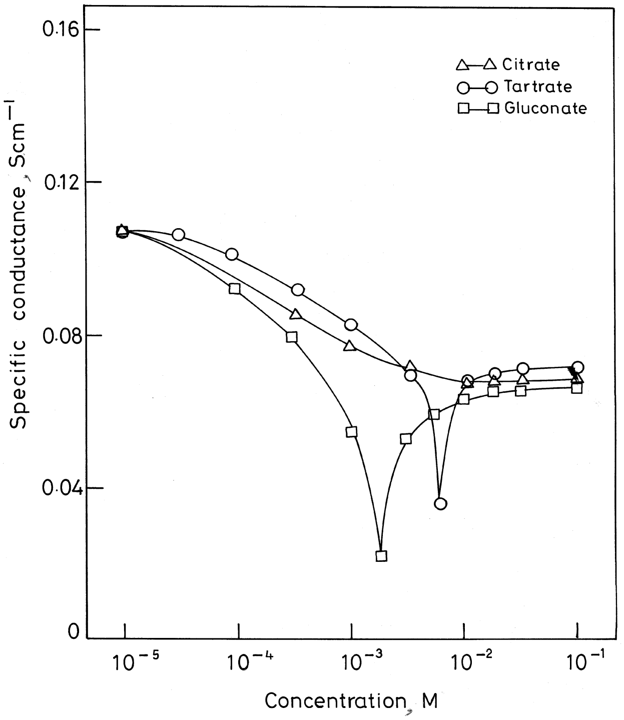

Fig. 4. Variation of specific conductance of zincate in the presence of additives.

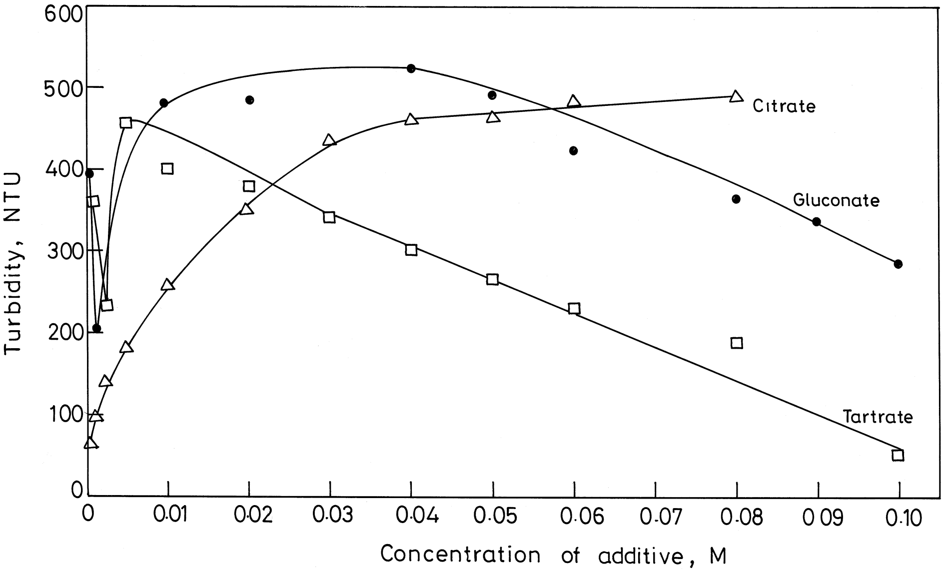

Fig. 5. IR spectra of gluconate and zincate gluconate compound.

are absent in the IR spectrum. The inference one gets from the spectrum is that most or all of the alcoholic groups are not free. This observation is very significant in the sense that gluconate has 5 OH groups and only one OH group viz., (α-OH) is expected to be involved in metal ion bonding. Melson and Pickering [11] who have made a study of the preparation and analysis of $Zn(OH)_3$glu suggested that several gluconate residues are joined by hydroxy species as proposed for the Al, Cr and Th compounds [12]. The IR spectrum of the tartrate compound (curve not shown) presented features that are very similar to that of gluconate compound. There were no free OH functionalities, confirming that several tartrate residues are joined by hydroxy groups.

X-ray and NMR analysis [13–15] have shown similarity in the binding features of tartrate and gluconate ions

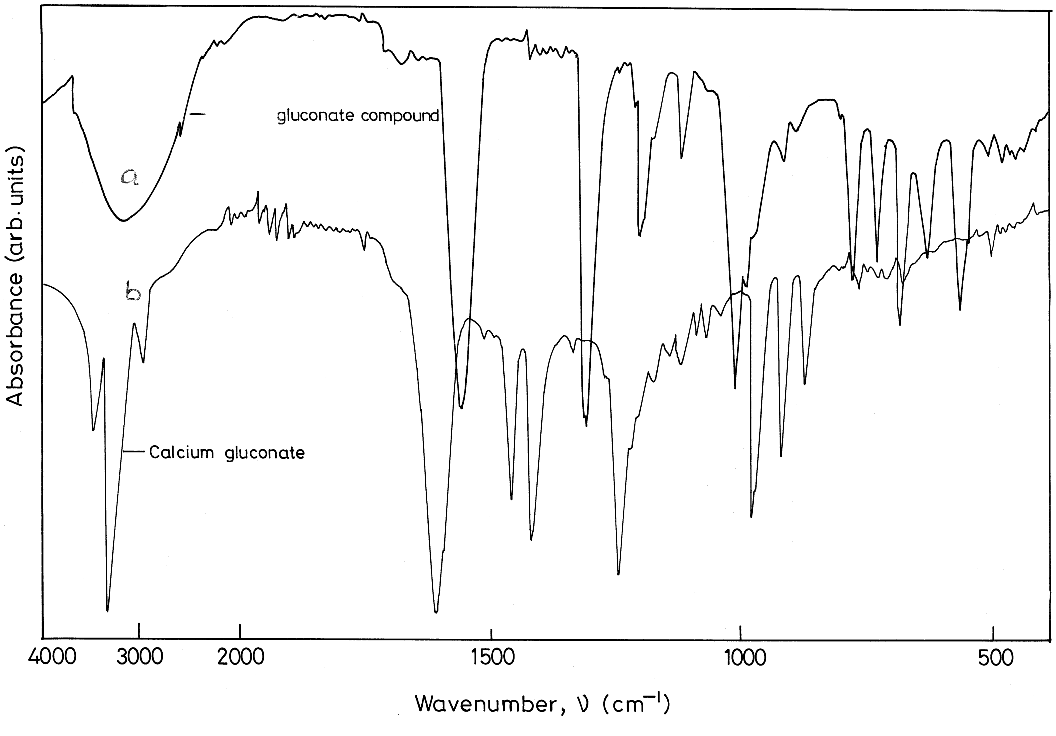

Fig. 6. Dependence of turbidity of zincate solution on the concentration of the additive.

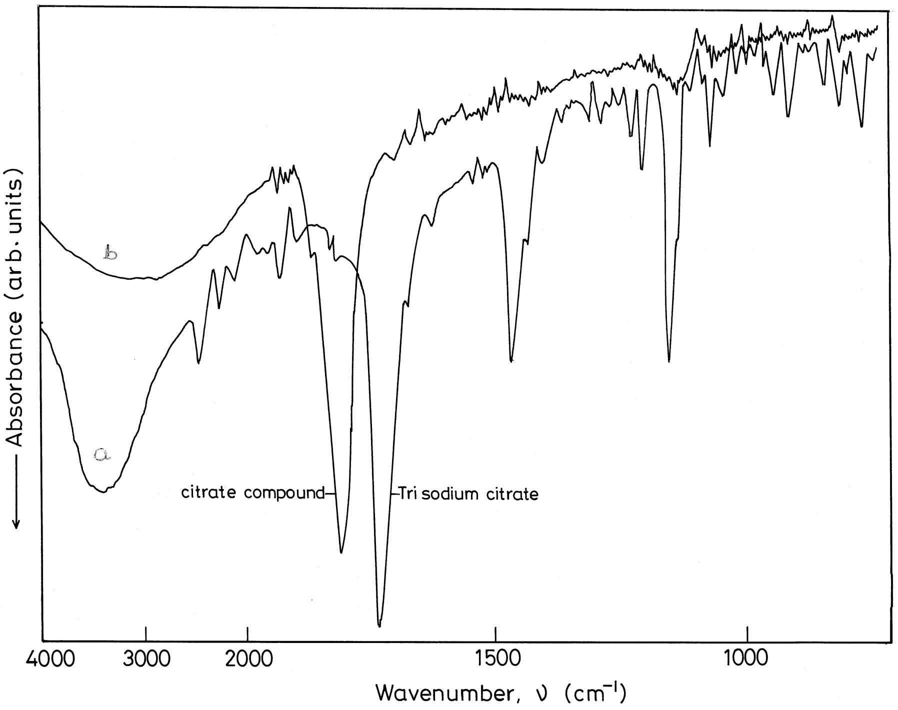

Fig. 7. IR spectra of citrate and zincate citrate compound.

towards metal ions. The C_2–O_2 bond (i.e., the hydroxyl group) lies approximately in the plane of the corboxylate group so as to occupy coordinate position around metal

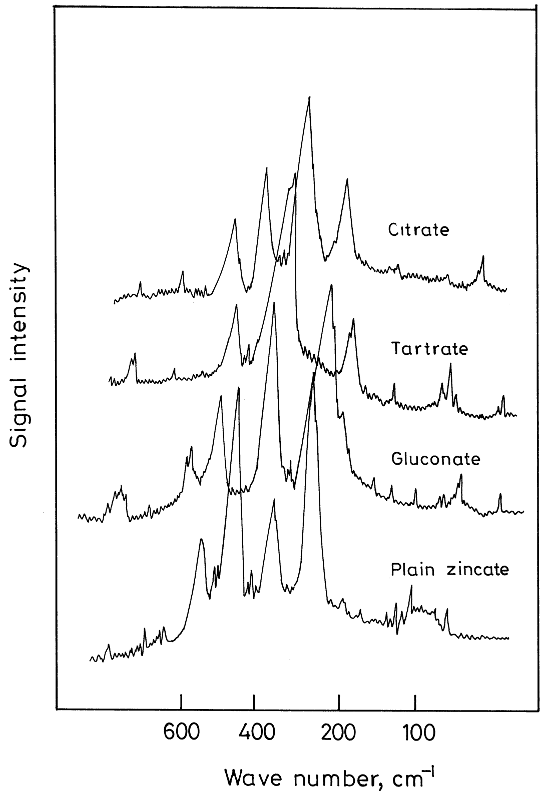

Fig. 8. Raman spectra of zincate in the presence of additives (i) sodium citrate, (ii) sodium potassium tartrate and (iii) calcium gluconate. Curve (iv) is the spectrum of plain zincate.

ion. The micelle formation for the additive action of silicate on ZnO in KOH solutions was proposed by Foller [16]. The adsorption of silicate on ZnO and its high negative charge leads to colloid formation due to repulsive

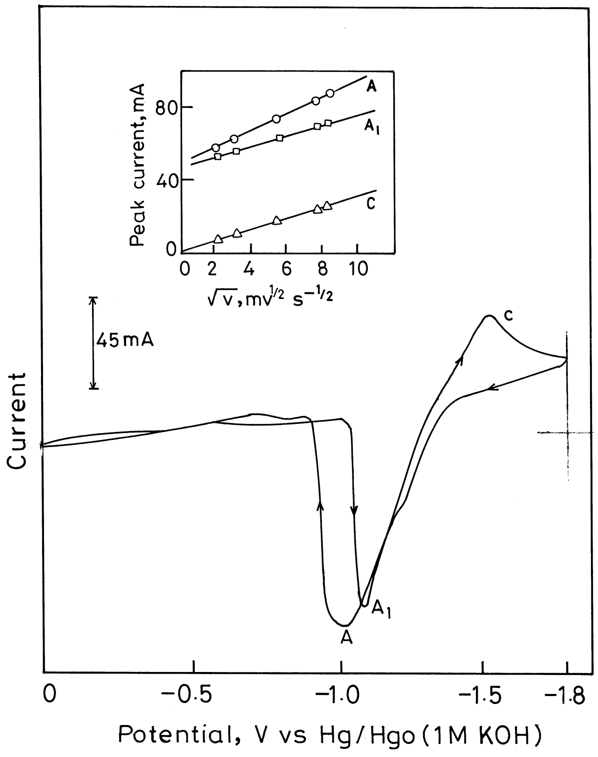

Fig. 9. Cyclic voltammogram for zinc in 3.0 M NaOH; sweep rate 100 mV S^{-1}. Inset shows effect of sweep rate on peak current.

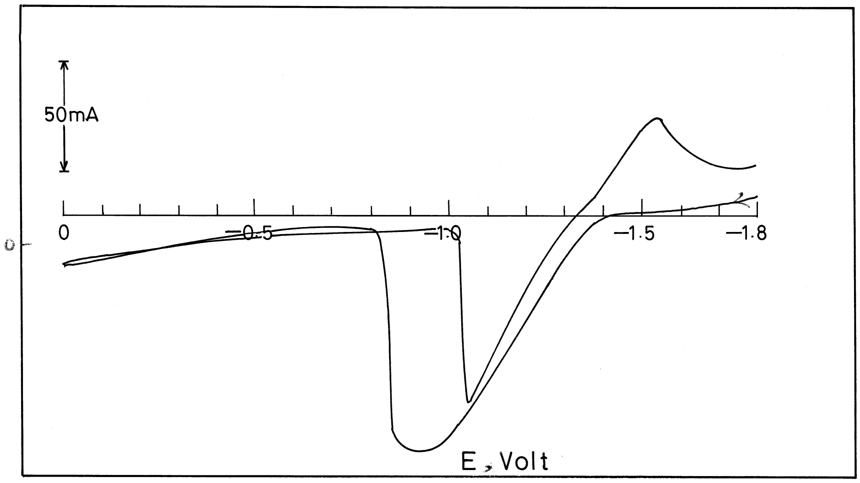

Fig. 10. Cyclic voltammogram of zinc in 3.0 M NaOH in the presence of 0.025 M citrate at a sweep rate of 70 mV s^{-1}.

forces between particles. It has been shown that silicate has the ability for potential coordination with each ZnO and surface oxygen because of the high charge density it can impart to a micelle. Flerov [17,18] argued that a more extensive hydration sheath around silicate further isolated each micelle from the hydroxide ion and the free water needed to dissolve it. Marshall et al. [19] concluded by conductivity studies that the number of ZnO molecule per colloidal particle may be of the order of five or six. Stannate and titanate have also been shown to behave similar to silicate.

As far as the interaction of gluconate with zinc hydroxide is concerned, it has been shown that gluconate can react with zincate by replacing one of the hydroxyl ligands to from [$Zn(OH)_3$(glu)] species in solution [20]. Such a species can form micellar aggregates in solution, like silicate, titanate or stannate compounds because it has been argued [21,22] that in the case of silicates, the terminal OH groups are responsible for the adsorption and colloidal phenomena observed in silicate added zincate solutions. Citrate possesses a single OH group; tartrate has two and gluconate has five OH groups. Logically, the tendency for micelle formation should be least for citrate. The conductance data (Fig. 4) reveal that the fall and rise in specific conductance typical of a CMC is observed with tartrate and gluconate. The effect is not pronounced in the case of citrate.

The turbidity data of citrate containing zincate do not show any sudden increase and decrease in particle size over the concentration range studied (Fig. 5). This observation supports the notion that micelle formation does not take place in the presence of citrate. A noteworthy observation made in the citrate case is that the citrate-added zincate turned yellow in colour with the increase in citrate concentration; further, citrate exhibited very high solubility in the zincate reaching about 2.7 M in concentration. Such a colour change or high solubility was not observed in the case of tartrate and gluconate. A study of the influence of carbonate ions [23] on Zn/30% KOH has indicated complexing of zincate ions by carbonate ions. The effect of citrate can be expected to be similar to that of carbonate ions and the three carboxylate functionalities should enable

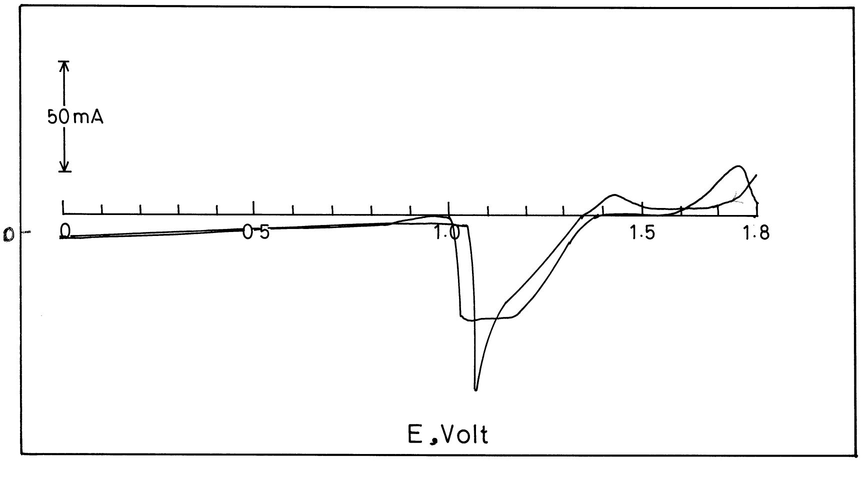

Fig. 11. Cyclic voltammogram of zinc in 3.0 M NaOH in the presence of 0.025 M citrate at a sweep rate of 5 mV s^{-1}.

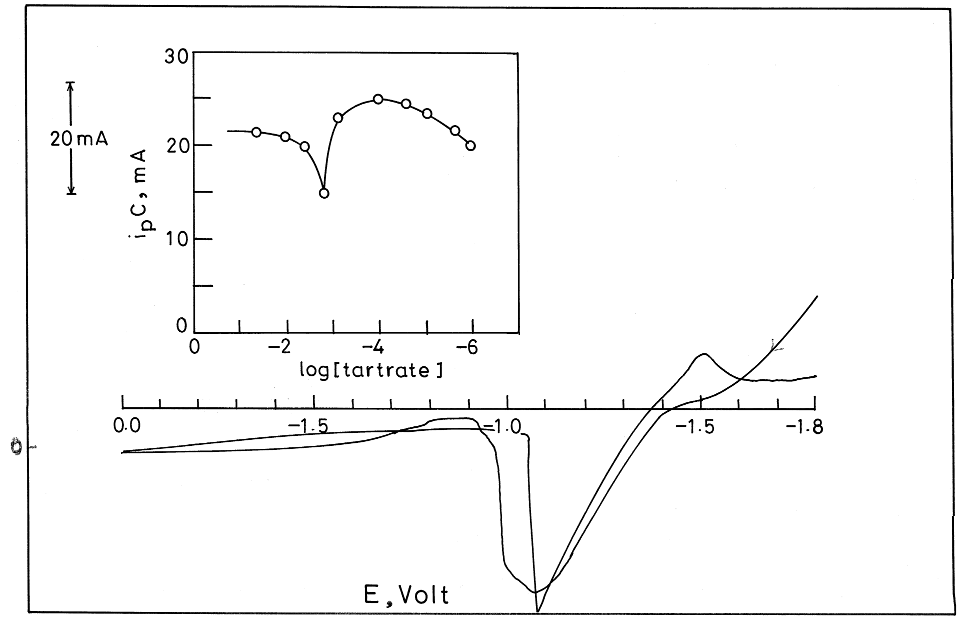

Fig. 12. Cyclic voltammogram of zinc in 3 M NaOH in the presence of 10 mM sodium potassium tartrate. $v = 30$ mV s^{-1}. Inset: variation of i_pC with [tartrate].

a facile complexation of zincate with citrate. In other words, citrate ions seem to help ZnO/$Zn(OH)_2$ to remain in solution in preference to a colloidal form.

Marshall et al. [17,18] observed greatly reduced hydrogen bonding in high concentration alkaline zincate solution via IR spectroscopy. A supersaturated zincate solution is thought to consist of three states [13,19]. They are: (i) individual zincate ions, (ii) an unstable colloidal state involving zinc oxide or hydroxide and (iii) a relatively stable polymeric state. It has been reported that additives like xylitol and molasses can stabilize polymeric zincate structure. It was proposed that hydrogen ions of zincate ions [19] may hydrogen bond to zinc oxide nuclei such that further nucleation and growth is suppressed. The net effect is that a lace-like polymeric structure of zincate and zinc oxide remains in solution.

It seems reasonable to expect complexation of zincate with citrate ions to form polymeric species in solution.

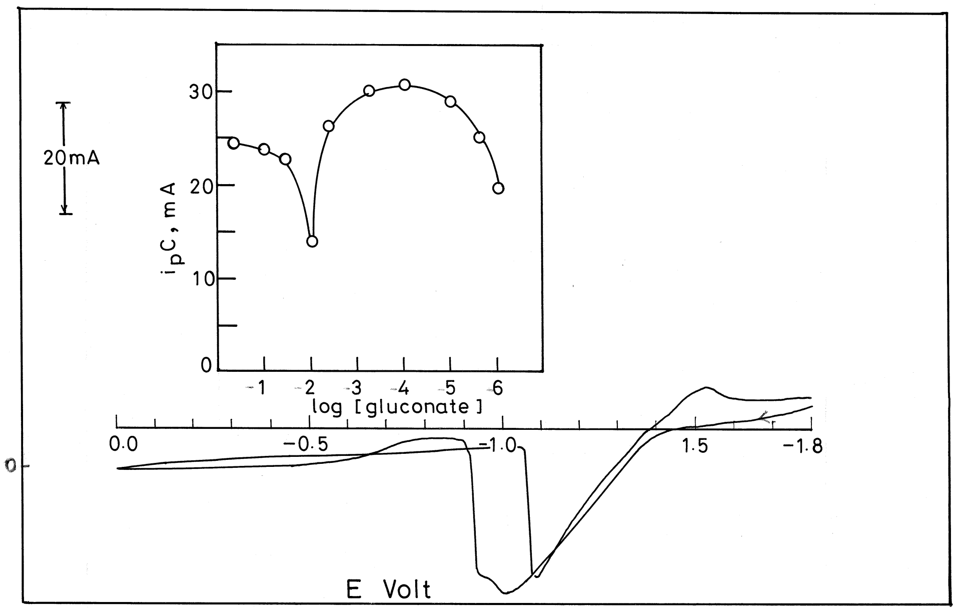

Fig. 13. Cyclic voltammogram of zinc in 3 M NaOH in the presence of 3 mM calcium gluconate. $v = 30$ mV s^{-1}. Inset: Variation of i_pC with [gluconate].

Table 1
Cyclic voltammetric data for the anodic dissolution and redepostition of zinc in 3 M NaOH in the presence of various concentrations of citrate at 30 mV s^{-1}

Citrate (M)	$i_p A$ (mA)	$i_p A_1$ (mA)	$i_p C$ (mA)	$E_p A$ (mV)	$E_p A_1$ (mV)	$E_p C$ (mV)	$\Delta E_p = E_p A - E_p C$ (mV)
0	63.0	60.0	15.0	− 950.0	− 1062.5	− 1500.0	550.0
0.0050	68.0	71.0	16.4	1000.0	1060.0	1470.0	470.0
0.010	73.0	80.5	19.2	1050.0	1062.0	1450.0	400.0
0.025	90.0	100.4	33.0	− 1122.5	− 1062.5	− 1467.5	345.0
0.050	102.0	120.8	27.0	− 1075.0	− 1075.0	− 1475.0	400.0
0.065	105.1	100.0	28.0	− 1050.0	− 1050.0	− 1475.0	425.0
0.120	108.8	120.8	32.0	− 1057.5	− 1050.0	− 1475.0	408.0
0.250	97.5	110.4	31.5	− 1075.0	− 1050.0	− 1487.5	412.5
0.500	84.0	104.3	33.0	− 1082.5	− 1087.5	− 1475.0	423.0
1.00	75.0	93.8	29.2	− 1100.0	− 1075.0	− 1500.0	400.0
2.00	66.5	80.0	30.6	− 1112.5	− 1100.0	− 1525.0	413.0

This expectation emerges from the following known facts. A study of the influence of aliphatic carboxylic acids on the buffering capacity and hydrate forming pH of zinc sulphate solutions indicated that citric acid extends the buffer region into the alkaline range and the region of solid phase precipitation increases to 9–11 [24]. The analogous behaviour of zincate and aluminate ions have been indicated with respect to formation of polymeric species [24,25] and it has been shown by Akira et al. [26] that chemical components like citrate combine with aluminium hydroxide to form coordination compounds. Citrates have also been found to effect masking of hydrolytic precipitation reaction of Al(III)/Ga(III)Th(III). IR, electronic and X-ray study of zinc(II) complexes of polycarboxylic acids such as citric acid, lactic acid malonic acid, malic acid and succinic acid has shown that most of these complexes are polymeric in structure in which the metal is in an octahedral D_4h environment; very often a sheet type polymer structure has been described [27–31].

3.2. IR and Raman spectral analysis

The IR spectrum of the compound isolated from the macrodissolution of zinc in presence of citrate (Fig. 7) confirms the complexation of citrate with zincate. The absorption characteristic of carboxylate ion at 1720 cm^{-1} in citrate shows a marked shift together with some decrease in the intensity in the zincate–citrate compound showing that the carboxylate groups are involved in bonding. Similarly, the bending mode of the OH functionality at around 1450 cm^{-1} is absent in the compound indicating that –OH is also involved in complexation.

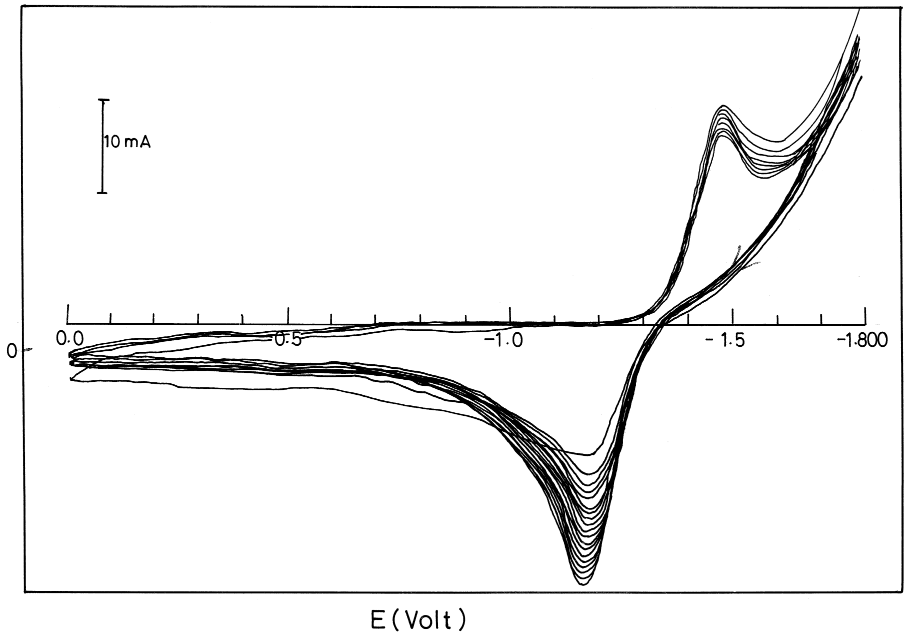

Fig. 14. Cyclic voltammogram of zinc oxide, in 3 M NaOH.

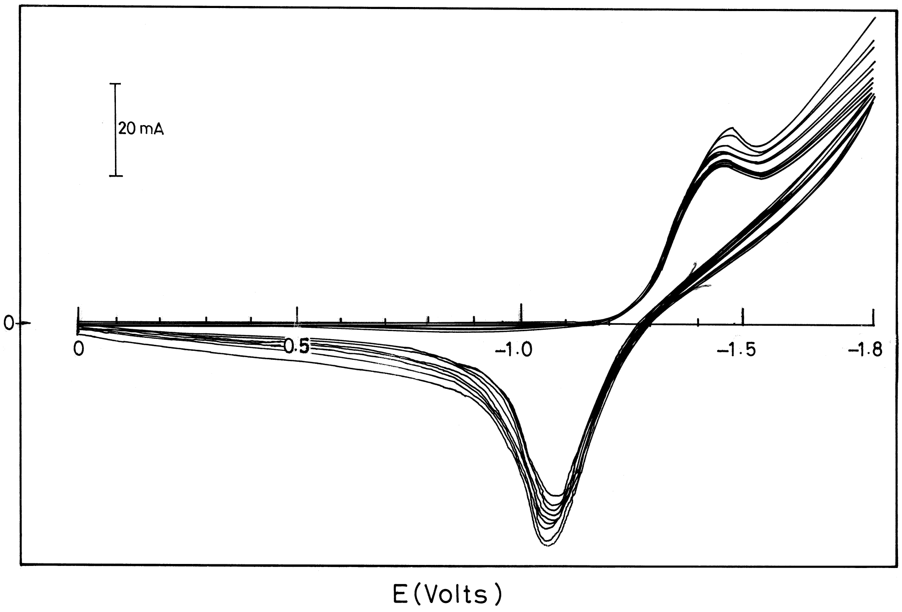

Fig. 15. Cyclic voltammogram of zinc oxide containing 10% citrate, in 3 M NaOH.

Raman spectra of the compounds of zincate with citrate, tartrate and gluconate are presented in Fig. 8. The spectrum of zincate–citrate compound is similar to that of zincate but the values are shifted to the shorter frequency region. A similar shift has also been reported in polymeric zincate structures [32,33]. Therefore, it can be reemphasized that citrate stabilizes a polymeric zincate structure [33]. The Raman spectra of the tartrate compound shows only three absorptions (500, 380, 185 cm^{-1}). Similarly, gluconate compound also shows only three absorptions but at values 580, 400 and 233 cm^{-1}. These observations confirm that tartrate and gluconate produce zincate compounds that are distinct from the product of zincate–citrate interaction. At the same time, each of the two compounds is distinct as seen from different Raman absorptions.

3.3. Cyclic voltammetry

Cyclic voltammogram for the dissolution and redeposition of zinc in 3 M NaOH is shown in Fig. 9, in which

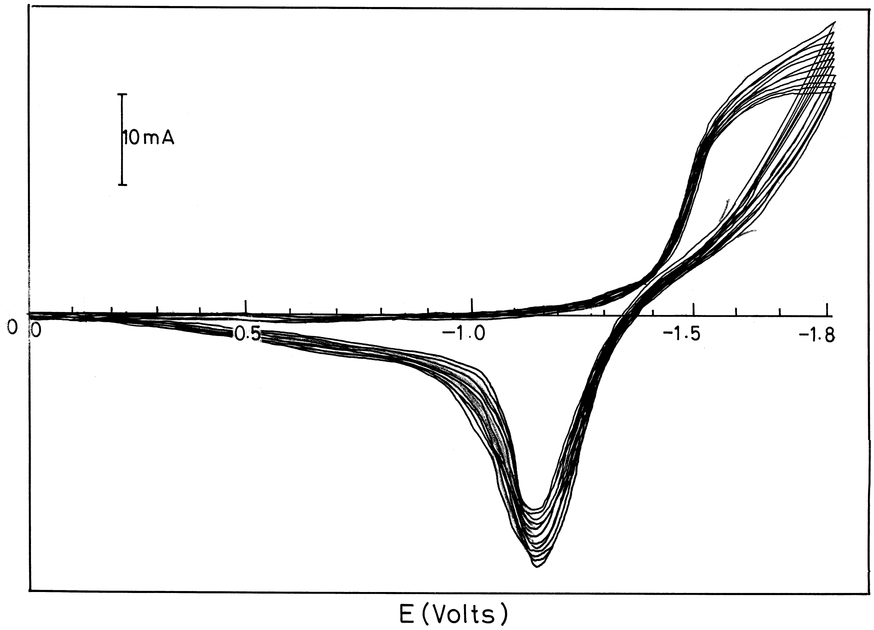

Fig. 16. Cyclic voltammogram of zinc oxide containing 10% tartrate, in 3 M NaOH.

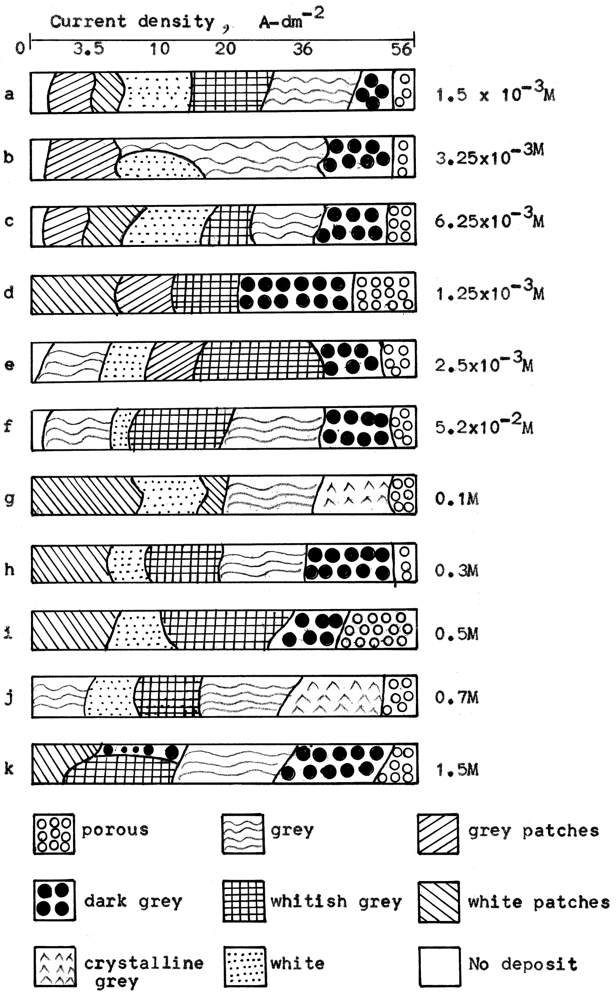

Fig. 17. Hull cell pattern of zinc deposition from zincate bath in the presence of various concentrations of sodium citrate.

peak *A* appearing on the positive going sweep corresponds to the anodic dissolution of zinc in the medium. Peak A_1, appearing in the reverse scan is due to the reestablished oxidation of zinc; peak *C* corresponds to the reduction of the electrode reaction product

The cyclic voltammograms in presence of the additives are shown in Figs. 10–13. In general, in the cyclic voltammogram of zinc in 3.0 M NaOH in the presence of citrate, the peak current values are higher than in the case of NaOH alone. On the other hand, the peak current values are lesser in both tartrate and gluconate. The greater magnitude of peak current observed in the case of citrate can be explained as follows. The anodic film in citrate is more porous and less coherent than the film formed in NaOH alone. Thus citrate seems to help $ZnO/Zn(OH)_2$ to remain in the solution in a complexed state.

E_pC is at minimum in a concentration of 0.025 M of citrate. Table 1 reveals that ΔE_p, the difference between $E_p A$ and E_pC, is at minimum in a concentration of 0.025 M of citrate. Further, I_pC is also considerably higher than that in NaOH alone. The cyclic voltammetric data on the effect of tartrate and gluconate reveal a different a pattern. The dependence of peak current on the concentration is similar in both cases, although, the variation is more pronounced in case of gluconate than in the case of tartrate. The break point of i_pC vs. concentration plot indicates a decrease in the availability of free electroactive species. Such a feature can be associated with the formation of micelles or premicelles because when an electroactive species undergoes micellization or aggregation, the phenomenon is expected to be reflected in the concentration dependent parameters like peak current [34]. The nature of micelles or aggregates formed, however, requires a separate investigation.

In order to gain an understanding of the effect of these additives on zinc electrode performance, we studied the cyclic voltammetric behaviour of zinc oxide electrode that incorporated these additives (Figs. 14–16). The cyclic voltammogram of zinc oxide (Fig. 14) shows a peak at

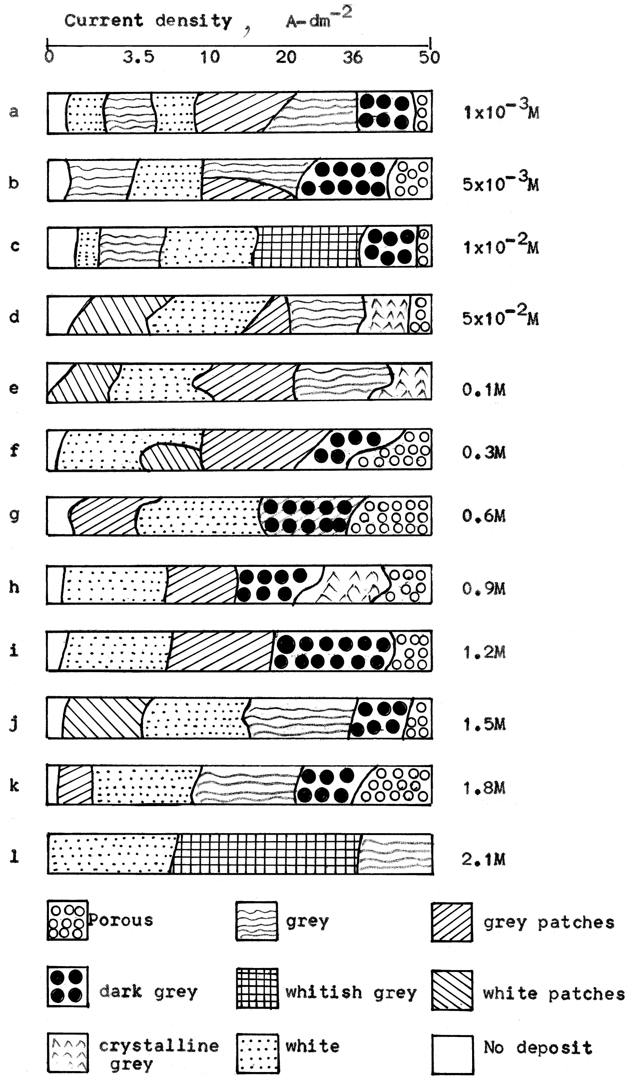

Fig. 18. Hull cell pattern of zinc deposition from zincate bath in the presence of various concentrations of calcium gluconate.

-1170 mV on the positive going sweep and a corresponding peak at -1470 mV on the negative going sweep. Incorporation of the additives brings about certain changes in the cyclic voltammetric features. The peak current of both anodic and cathodic processes is higher in the case of citrate than in the absence. On the other hand, in the case of both tartrate and gluconate the i_p values are lower. The effect of multiple cycling has been studied. The area covered under the cyclic voltammetric peak $(i \times t)$ indicates some difference for the additives. In the case of citrate, the voltammogram showed only slight changes in area after several cycles which shows that the electrochemical reaction occurs steadily in the system. For tartrate and gluconate there was some reduction in the peak areas.

3.4. Electrodeposition of zinc from zincate bath

Hull cell patterns of zinc plating produced in the presence of the additives are shown in Figs. 17–19. Tartrate produces a good deposit over a wide range of current density and the effect is prominent in the higher concentration range, viz. 0.1–0.2 M. Gluconate also gives a good deposit over a wide current density range and the effect is prominent at a gluconate concentration of 0.3–0.7 M. In presence of citrate, there is no significant variation in the morphological features with respect to change in concen-

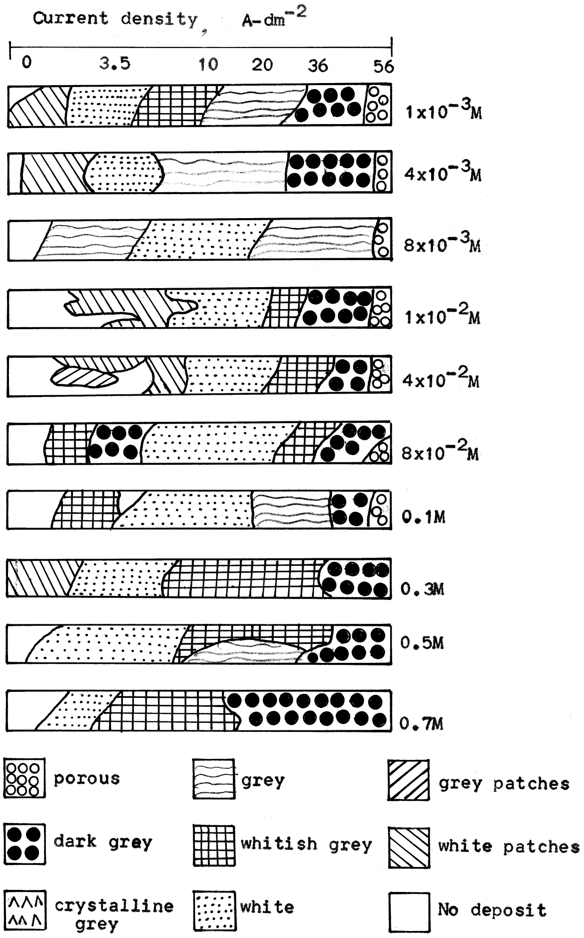

Fig. 19. Hull cell pattern of zinc deposition from zincate bath in the presence of various concentrations of potassium sodium tartrate.

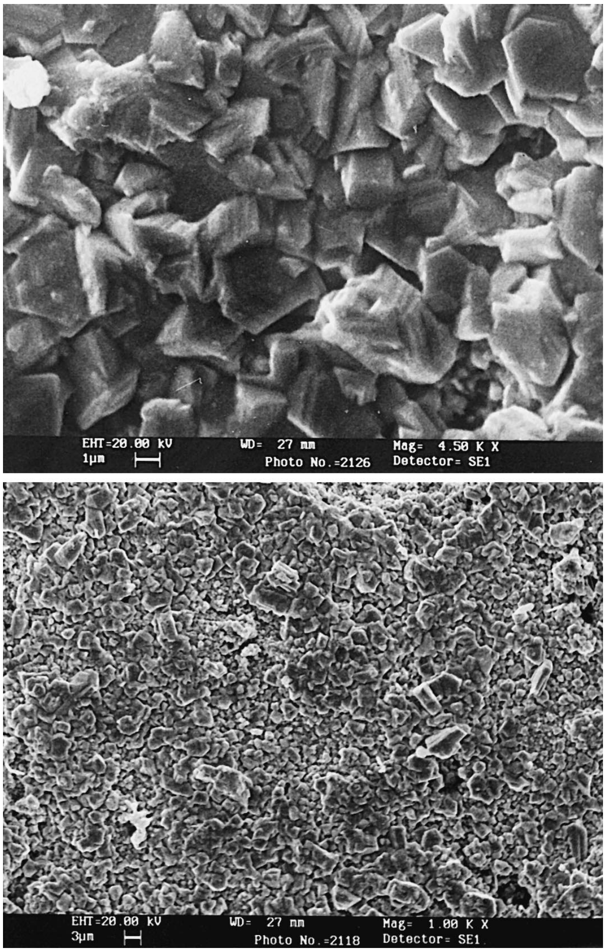

Fig. 20. SEM pictures of white zinc deposit obtained in the presence of tartrate.

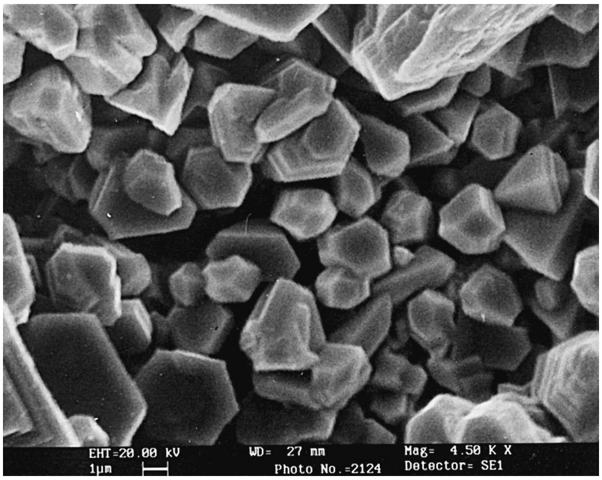

Fig. 21. SEM picture of grey zinc deposit obtained in the presence of tartrate.

tration of 0.3–0.7 M. Zinc crystallizes in hexagonal unit lattice. The morphology of an electrodeposit depends on how the unit lattice develops. An examination of the Hull cell pattern with naked eye does not give much information on the morphology of the deposit. Henceforth, different zones in the Hull cell pattern were examined by SEM pictures. In this analysis, three morphological types viz., white, grey and crystalline, have been selected because of their relevance to the morphology of zinc electrode during charging. SEM pictures of white, grey and crystalline zinc deposits obtained from 0.1 M tartrate containing zincate are presented in Figs. 20–22. In the case of white deposit, the zinc nuclei are almost identical in size with uniform hexagonal morphology and one can observe (Fig. 20) a complete covering of the electrode surface. The grey deposit also contains nuclei of hexagonal plate-like morphology. However, most often the nuclei coalesce together to form spherical granules with different hexagonal faces. The spherical granule is only the result of a plate-over-plate layer growth with slight variation (± 2 μm) in the area of the aggregating plates. Bigger crystallites are scarcely seen. The variation in the size of the nuclei, though, small is reflected in the surface coverage of the substrate; internuclear voids are obvious (Fig. 21). The crystalline deposit shows a large variation in the size of the nuclei ranging from very small spherical granules through layered crystallites of medium size to large crystallites (Fig. 22). This variation results in a striated morphology (hills and valleys). There is some degree of difference between the grey and crystalline deposit with respect to layer growth. Whereas the layer development is even and coplanar in the former, the growth is somewhat puckered in the latter. Occasionally, symmetrical hexagonal configuration is lost and a tendency for elongated pyramidal growth is instilled. The SEM morphological features were similar for both tartrate and gluconate additive action. In the case of citrate, the crystalline deposit was somewhat coarser than that obtained in presence of the former additives.

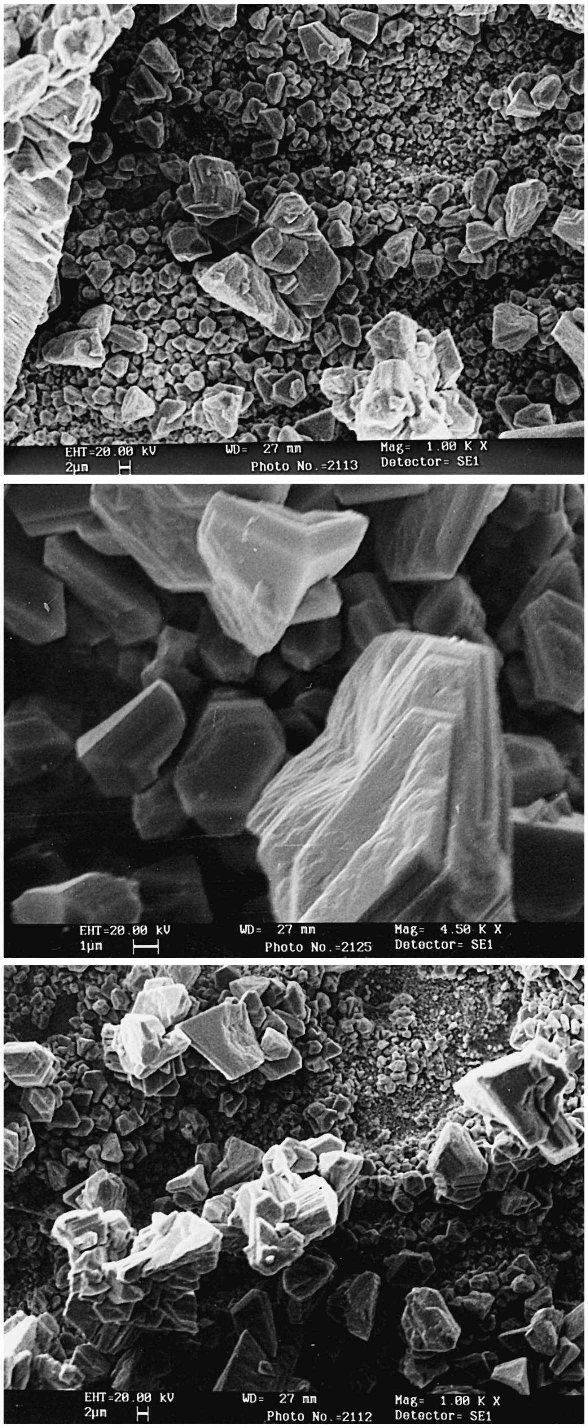

Fig. 22. SEM pictures of crystalline zinc deposit obtained the in presence of tartrate.

4. Conclusion

The decrease in zinc oxide solubility in the presence of additives follows the order gluconate > tartrate > citrate. Specific conductance of additive containing zincate is generally less than that in the absence of the additives. In the case of both tartrate and gluconate, there is a fall and then a rise in the conductance values with respect to concentration. A minimum point is seen on the conductance vs. concentration plot indicating micellization/aggregation phenomena in the presence of these additives. Turbidimetric analysis of zincate made in the present study has provided supportive evidence for the occurrence of such events. Spectral studies confirm compound formation of zincate with gluconate and tartrate whereas citrate is shown to enter into intermolecular association with zincate stabilizing a polymeric zincate structure. Multiple cyclic voltammetry of zinc oxide electrode indicates greater charge retention for citrate than for the other additives. The results indicate that citrate could prove useful both as an electrolyte additive as well as an electrode additive for zinc based cells.

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