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Interaction of zincate with additives turbidimetric, IR and Raman spectral analyses

R. Renuka*, S. Ramamurthy, L. Srinivasan[1]

Central Electrochemical Research Institute, Madras Unit CSIR Madras Complex, Chennai-600 113, India

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Abstract

The interaction of zincate with additives, viz., alkaline earth oxides, cadmium oxide, nickel hydroxide, cobalt hydroxide bismuth oxide, sodium carbonate, and lithium hydroxide is investigated by turbidimetry and Raman spectroscopy. From the pattern of dependence of turbidity on additive concentration, the additives can be classified into three groups: (i) BeO, CdO, MgO, $Ni(OH)_2$, $Co(OH)_2$; (ii) CaO, BaO, SrO; (iii) LiOH, Bi_2O_3, Na_2CO_3. An identical grouping of additives has been discerned from Raman spectral analysis. Turbidimetry is a simple inexpensive technique for understanding the processes taking place between the additives and the zincate solution. Products of electrochemical dissolution of zinc in 4 M NaOH containing alkaline earth oxides, SnO, CdO, $Ni(OH)_2$, $CO(OH)_2$, or LiOH have been analysed by IR spectroscopy. The effect of heat treatment of the products on IR spectral pattern is described in the light of thermogravimetric analysis.

Keywords: Zincate; Zincate additives; Turbidimetry of zincates; Raman spectra of zincates; IR spectra of zincates

1. Introduction

Employment of inorganic additives in the electrolyte of Zn/NiOOH cells is well known [1–6]. Additives such as CdO, Bi_2O_3, and Na_2CO_3 have been shown to be beneficial to the performance of zinc–alkaline cells [7–13]. The influence of $CaO/Ca(OH)_2$ on zincate has also been investigated [14–18]. Other alkaline earth oxides, however, have not been studied. The present investigation aims to understand the nature of zincate in the presence of certain inorganic additives, viz., alkaline earth oxides, CdO, LiOH, Bi_2O_3, and Na_2CO_3. NaOH (4 M) is chosen as the electrolyte because the nature of the zincate species present in this solution is known with certainity [19]; also this electrolyte is commonly used for zinc electrodeposition.

2. Experimental

Turbidimetric examination was made using a Systronics Nephleomeltry turbidimetry meter which has the provision to measure four different turbidity regions, namely: 0–10, 10–100, 1000–10 000.

Preparation of zincate and the additives has been described elsewhere [2]. The equipment for Raman spectroscopy consisted of an argon-ion laser and a Jarrel-Ash 1-mm double monochromater followed by a photon counting assembly. Samples were filtered through a G4 sintered crucible before placing in the cell (1 cm quartz) for measurement. After each run, the cuvette was cleaned by immersion in HCl followed by thorough washing with distilled water. Before each experiment, the cuvette was washed with the solution to be used. For each measurement, the absence of carbonate was ensured by running the spectrum for the band at 1065 Δ cm^{-1} which is characteristic of carbonate.

In order to isolate the products formed during the anodic dissolution of zinc in 4 M NaOH in the presence of the additives, macrodissolution of zinc was carried out in 4 M NaOH containing 5 mM of the additives at a constant potential of −1000 mV vs. Hg/HgO (1 M KOH). This potential was chosen on the basis of the cyclic voltammetric behaviour of zinc; all the alkaline earth oxides and LiOH showed a major dissolution process at −1000 mV vs. Hg/HgO (1 M KOH). (The cyclic voltammetric study is discussed in Ref. [20]). A zinc sheet (99.9% pure) of

* Corresponding author. Fax: +91-44-2352-456.

[1] Postgraduate student of the Department of Chemistry, Loyola College Autonomous, Chennai-600 034, India.

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Table 1
IR absorption frequencies of products of anodic dissolution of zincate in 4 M NaOH medium in presence of additives (in cm^{-1})
(s) = strong, (w) = weak.

Reactants		Products	
$Ba(OH)_2$	3610 (s)	BeO + zincate	3850 (s) 950 (s)
$Sr(OH)_2$	3600 (s)	MgO + zincate	3880 (s)
$Mg(OH)_2$	3750 (s)	CaO + zincate	3500 (s)
$Be(OH)_2$	3550 (s)	BaO + zincate	3780 (s)
$Ca(OH)_2$	3500 (s)	LiOH + zincate	3500 (s) 1100 (w)
$Zn(OH)_2$	3720 (s)	LiOH + zincate (1375 mV)	1209 (s)
$Cd(OH)_2$	3735 (s)		
$Ni(OH)_2$	3600 (s)	SrO + zincate	3700 (s)
$Co(OH)_2$	3600 (s)	SnO + zincate	3830 (s)
$Sn(OH)_2$	3700 (s)	$Co(OH)_2$ + zincate	3760 (s)
NaOH	3540 (s)	$Ni(OH)_2$ + zincate	3770 (s)
KOH	3550 (s)	$Ni(OH)_2$ + zincate	3760 (s)
LiOH	3700 (s)		3770 (s)

dimensions $0.01 \times 0.01 \times 0.003$ m was used and the solution was deaerated before commencing the dissolution. The current applied was 0.04 mA cm^{-2}. During zinc dissolution, the solution was continuously stirred with a magnetic stirrer while nitrogen was bubbled at a slow rate to maintain an inert atmosphere. Under these conditions, no passivation was observed [21]. Dissolution was terminated after 0.5 h and the solution was cooled to about 278 K for 4 h, allowed to stand at ambient temperature until the temperature reached about 293 K, and then filtered. The solid residue was first washed 10 times with 5% NaOH followed by repeated washing with double-distilled water and then dried in vacuum. This process of dissolution of zinc and isolation of products was continued (each time with a fresh bath containing the additives) until sufficient quantity of the product had been collected. For LiOH, the macrodissolution was also separately carried out at −1375 mV vs. Hg/HgO (1 M KOH) since cyclic voltammetry revealed an additional dissolution process at this potential. The IR spectra were recorded on a Shimadzu IR 408 spectrophotometer using KBr pellets. Thermogravimetric analysis was conducted with a Delta series TGA 7 instrument.

3. Results and discussion

3.1. IR spectral analysis of products of electrochemical dissolution of zinc in 4 M NaOH

All the compounds prepared in the present study exhibit a strong absorption in the region 3500–3700 cm^{-1} which

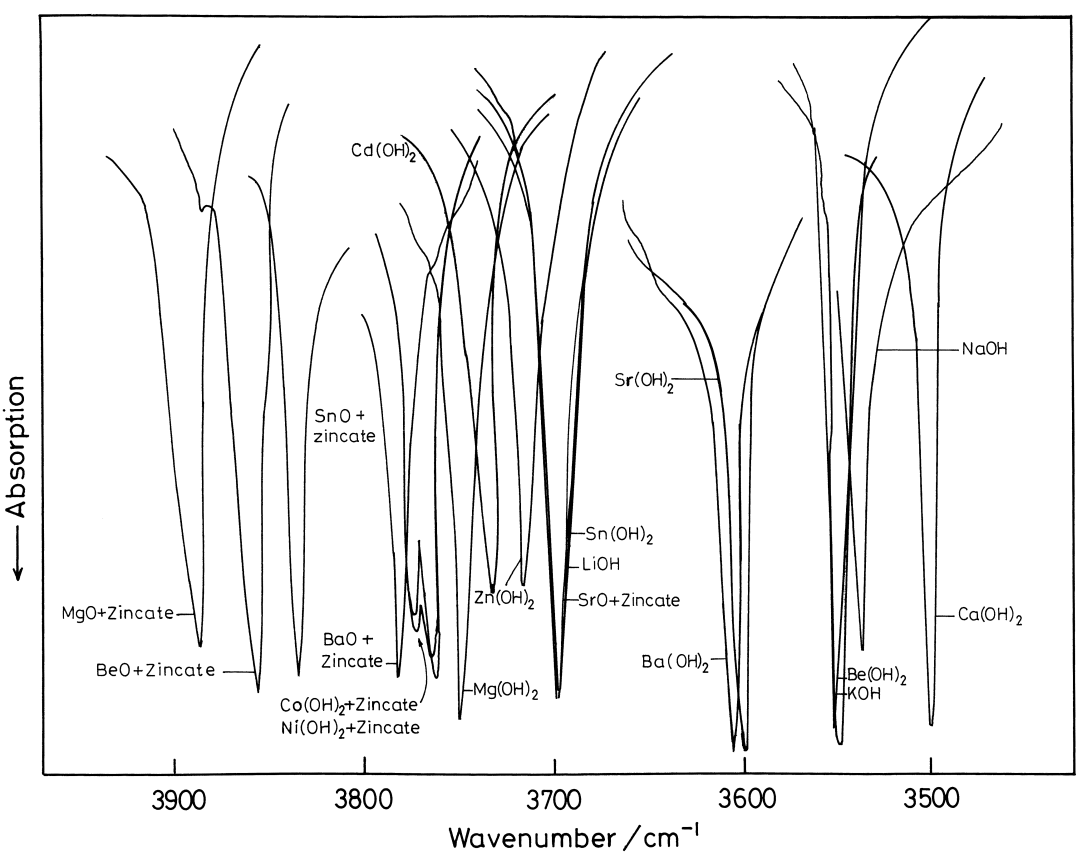

Fig. 1. IR spectra of anodic dissolution product(s) of zinc in 4 M NaOH in presence of additives.

indicates the presence of hydroxide (OH) groups [21]. The characteristic IR absorption frequencies of the products obtained for each additive along with that of the reactant hydroxide are presented in Table 1 and Fig. 1. It is evident from the data that absorption frequencies of the products are distinct from that of the corresponding hydroxide of the reactant and show a marked shift to higher frequency values which are indicative of bonding [22].

In the cyclic voltammogram (Fig. 2), LiOH exhibits two anodic dissolution processes. One of the processes is the common single dissolution process exhibited by the other additives, whereas an additional process was revealed at a more negative potential ($E_p = -1375$ mV). Therefore, the anodic dissolution products of both the processes were separately collected and analyzed. The IR spectrum of the product collected at -1375 mV, in the case of LiOH additive (Fig. 3) did not show any frequency characteristic of hydroxide or hydroxo complexes. On the contrary, a strong absorption at 1209 cm^{-1} was observed (Fig. 3) together with a strong absorption in the far IR region at 120 cm^{-1} (Fig. 4, curve c). Generally, oxide lattices show absorption around 1000 and 100–120 cm^{-1} [23]. Therefore, this product obtained from LiOH could be an oxide. Literature evidence [15] suggests that lithium can in fact form lithium oxozincate, e.g., $KLiZnO_2$. Such a compound, though a zincate in terminology, lacks OH functionality. Yet another zincate, viz., $Li_2[ZnO_4]$, is also known [16]. Therefore, either of these compounds might have been formed at -1375 mV.

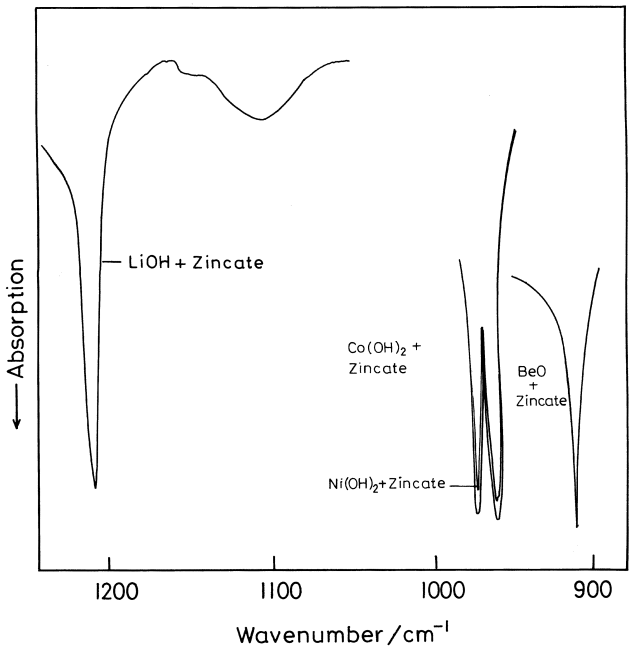

Fig. 3. IR spectra of anodic dissolution product(s) of zinc in 4 M NaOH in presence of additives.

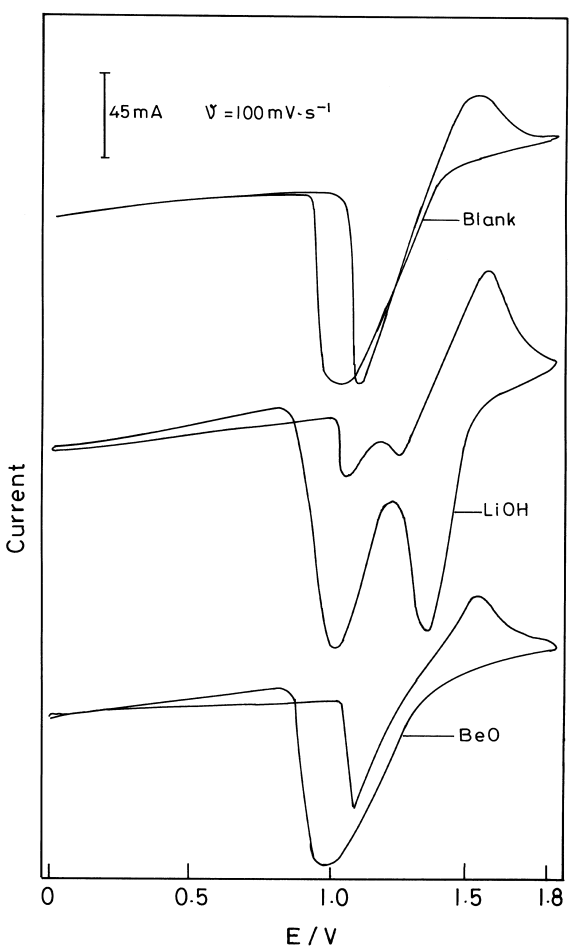

Fig. 2. Cyclic voltammogram for dissolution and redeposition of zinc in 4 M NaOH in presence of (a) 5 mM LiOH and (b) 5 mM BeO.

3.1.1. Effect of heat treatment on IR pattern

Since zincates, in general, are hydroxo complexes, and in the case of lithium, it was possible to observe the formation of both hydroxo and oxo compound, it is of relevance to examine the effect of heat treatment on the composition of the product because of the well-known hydroxide to oxide conversion. Since an IR spectrum can readily differentiate between hydroxo complexes, aqua-complexes, oxides, and hydrated salts, an attempt was made in the present study to examine the effect of heat treatment on the IR pattern. Generally, the hydroxo bridged nature of a compound or a complex is revealed by absorption around 950 cm^{-1} [22]. Therefore, the absorption at 950 cm^{-1} exhibited by the BeO compound (product formed at -1000 mV) indicates that it is a hydroxo bridged compound. Further, it is observed that heat treatment at 393 K for 6 h reduces the intensity of the peak characteristic of the bridged OH group (Fig. 4, curve a) with a concomitant development of a peak at 1100 cm^{-1} (Fig. 4, curve b), which is very prominent in the spectrum of the compound that has been heat treated at 393 K for 8 h. The far-IR absorption at around 130 cm^{-1} is also very clearly observed in the spectrum (Fig. 4, curve c).

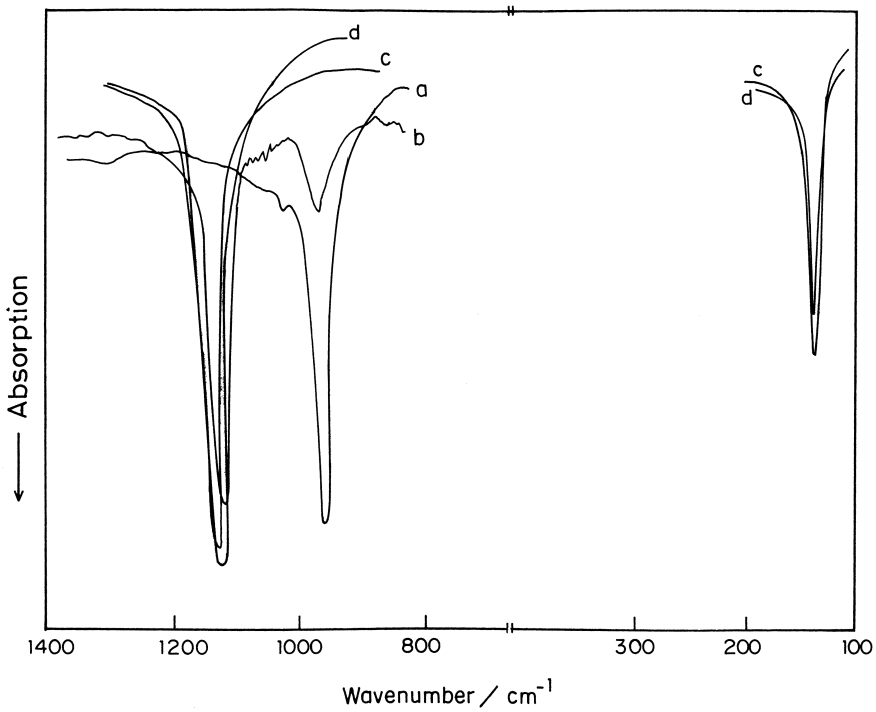

Fig. 4. Effect of heat treatment on IR and far-IR pattern of the product of anodic dissolution of zinc in 4 M NaOH in presence of LiOH. Temperature and time of heat treatment: (a) nil; (b) 393 K, 6 h; (c) 393 K, 8 h. Curve (d) is the IR spectrum of the BeO product.

Hartert and Glemer [24] studied the position of hydrogen in the lattice of crystalline hydroxides by the dependence of the IR absorption maximum on the OH radius. They found an exceptional behaviour of zinc hydroxide and beryllium hydroxide and that there is abnormal polarization of OH groups in these hydroxides, and the 'H' of the 'OH' is in resonance between two O atoms. It can therefore be concluded that prolonged heating of the product of BeO at 393 K lowers the distance of the two OH groups until an oxide is eventually formed. The readiness with which the bridged hydroxo compound is converted into an oxide by mild heating suggests certain other favourable factors of this effect. Foremost among such factors is the solubility of ZnO in BeO.

ZnO has an hexagonal (Wurtzite) lattice with the following cell parameters: $a = 3.24$ Å, $c = 5.19$ Å [25]. Among the commonly occurring metal oxides, only beryllium oxide (BeO) has hexagonal structure. Its lattice parameters are: $a = 2.69$ Å, $c = 4.3$ Å [26]. Even though the difference between the sets of parameters is somewhat greater than 15%, BeO and ZnO do appear to form a solid solution for which conductivity and X-ray diffraction measurements have been made [27]. The formation of a solid solution of ZnO with BeO in the present study was confirmed by the effect of ageing on precipitation. When the BeO-containing 4 M NaOH solution, into which electrochemical dissolution of zinc was carried out, was allowed to stand for 24–36 h, a crystalline compound separated out and gave a positive result in tests for the presence of both zinc and beryllium. The corresponding IR spectrum (Fig. 4, curve d) showed strong absorption at 1108 and 115 cm^{-1} in the far-IR region. In the present context of solid solution formation, it is worth mentioning that coprecipitation and hydrolytic synthesis have gained importance as techniques for preparing solid solutions [28–30].

Diadochy rather than isomorphism is the primary criterion in solid solution formation, so that a hexagonal compound may form a solid solution with a non-hexagonal one if the ionic sizes are correct [31]. Substitution of one cation for another in a particular lattice is often possible if the difference in the ion sizes is less than about 15%. Using this criterion and Pauling's empirical values for crystal radii [32], the following ions may be diadochic in oxide structures: Zn, 0.74 Å; Co, 0.74 Å; Ni, 0.72 Å. This is born out also by the fact that in minerals, zinc ions are often replaced by cobalt and nickel ions. The crystal structure and cell parameters of the oxides of these metals are as follows. CoO: cubic $a = 4.25$ Å [33]'; NiO: cubic, 4.17 Å [34]. IR spectra of the products of anodic dissolution of zinc in 4 M NaOH in presence of $Ni(OH)_2$ and $Co(OH)_2$ indicated crystalline compounds and gave positive results for the presence of zinc plus nickel or cobalt. In the IR spectrum, each of the compounds showed a doublet in the 3700–3800 cm^{-1} region (Fig. 1). A doublet is also seen in the 920–980 cm^{-1} region (Fig. 3). The appearance of a doublet is due to two different bonding sites for the OH groups in the lattice; one at zinc and the other at nickel or cobalt. Information available in the

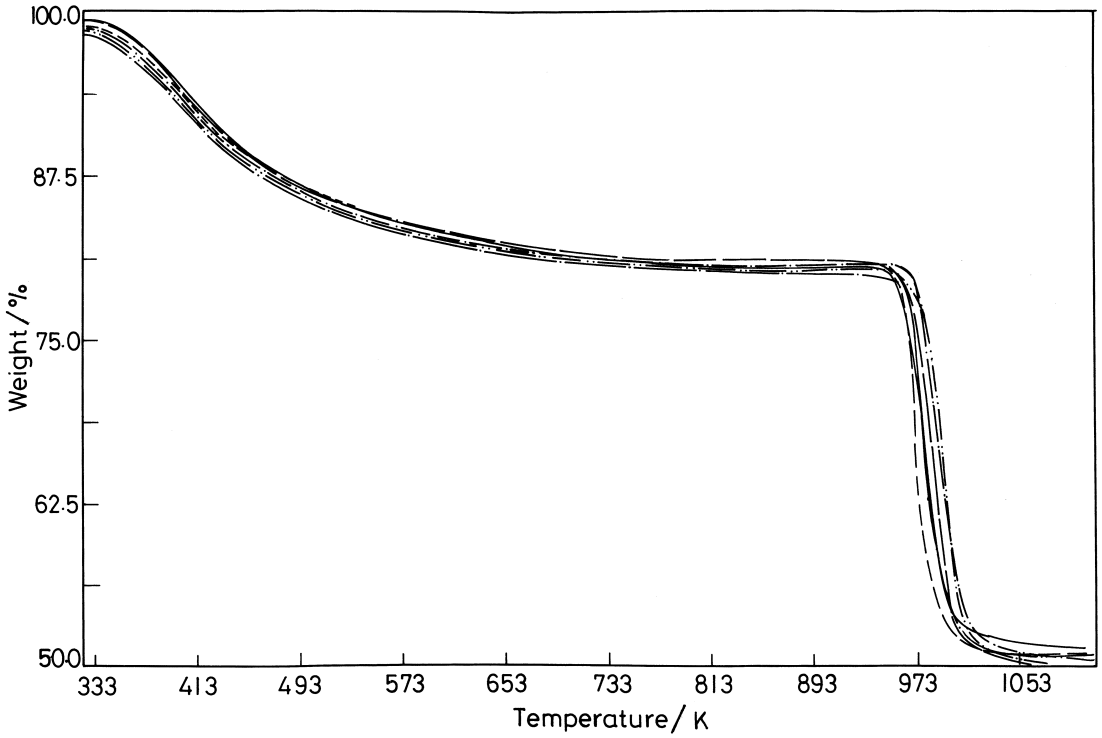

Fig. 5. Thermogravimetric curves of equimolar mixtures of ZnO with CdO, MgO, SnO, BeO, NiO, and CoO.

literature suggests that $Ni(OH)_2$ and $Co(OH)_2$ are excellent host lattices for $Zn(OH)_2$ [35–40]. It is imperative, therefore, from the IR data that $Zn(OH)_2$ forms solid solutions with $Ni(OH)_2$ and $Co(OH)_2$.

Unlike the BeO compound, the compound formed by electrochemically dissolving zinc with $Ni(OH)_2$ and $Co(OH)_2$ does not exhibit any change in the IR spectrum due to mild heating (393 K). On the other hand, heating at

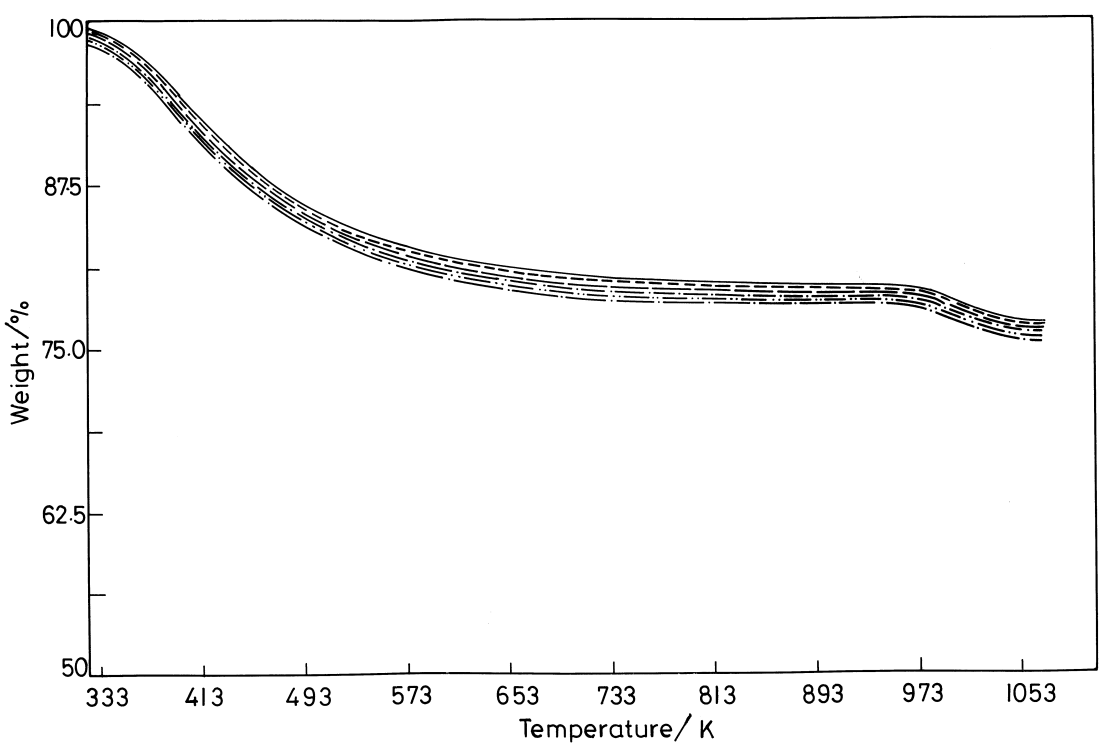

Fig. 6. Thermogravimetric curves of aged product of anodic dissolution of Zn in 4 M NaOH which contains CdO, MgO, SnO, BeO, $Ni(OH)_2$, or $Co(OH)_2$.

723 K leads to disappearance of OH linkages with the appearance of prominent absorption, owing to oxide linkages at 1100 and 108 cm^{-1} in the far-IR region. Qualitative analysis indicates the presence of both zinc and nickel (or cobalt). Thus, it can be inferred that the hydroxide solid solution has been converted into an oxide solid solution. In other words, solid solution formation does take place between zinc and nickel or cobalt in the hydroxide states, as well as in the oxide states.

Compounds of MgO, CdO, and SnO with electrochemically dissolving zinc in 4 M NaOH exhibit similar IR patterns in that they do not indicate the presence of bridged OH, (i.e., absence of absorption at 950 cm^{1}). Further, they do not show any doublets for the OH absorption modes. In this way, they differ from the compounds of BeO, $Ni(OH)_2$, or $Co(OH)_2$. Upon mild heating at 393 K for 10–12 h, however, absorption characteristics of the formation of an oxide are indicated (110–150 cm^{-1}). Cell parameters are favourable for the formation of solid solution of ZnO in MgO, CdO, or SnO [41]. Nephelometric analysis of zincate [42] and battery discharge studies [43,44] conformed solid solution of ZnO in MgO, CdO, and SnO. Supportive evidence for the formation of solid solutions of ZnO with CdO, MgO, BeO, $Co(OH)_2$, $Ni(OH)_2$, or SnO is provided by thermogravimetric analysis (Figs. 5 and 6).

Mild heat treatment of the product of anodic dissolution of zinc in the presence of BaO, SrO, and CaO does not cause changes in the IR pattern. It is therefore inferred that these products prefer to remain as hydroxides (zincates). The LiOH compound (−1000 mV) exhibited a change in the IR pattern due to heating. The absorption at 3500 cm^{-1} disappeared upon treatment at 473 K for 4 h, while a peak with a strong absorption at 1100 cm^{-1} (spectra not shown) appeared and suggested the conversion of hydroxozincate to an oxozincate.

3.2. Turbidimetry

The dependence of turbidity of doped zincate solutions on the additive concentration is shown in Fig. 7. Based on the general trends, the additives can be classified into three groups. These are: (i) BeO, CdO, MgO, $Ni(OH)_2$, $Co(OH)_2$; (ii) CaO, BaO, SrO; (iii) Bi_2O_3, LiOH, Na_2CO_3. Exactly the same classification was revealed by other

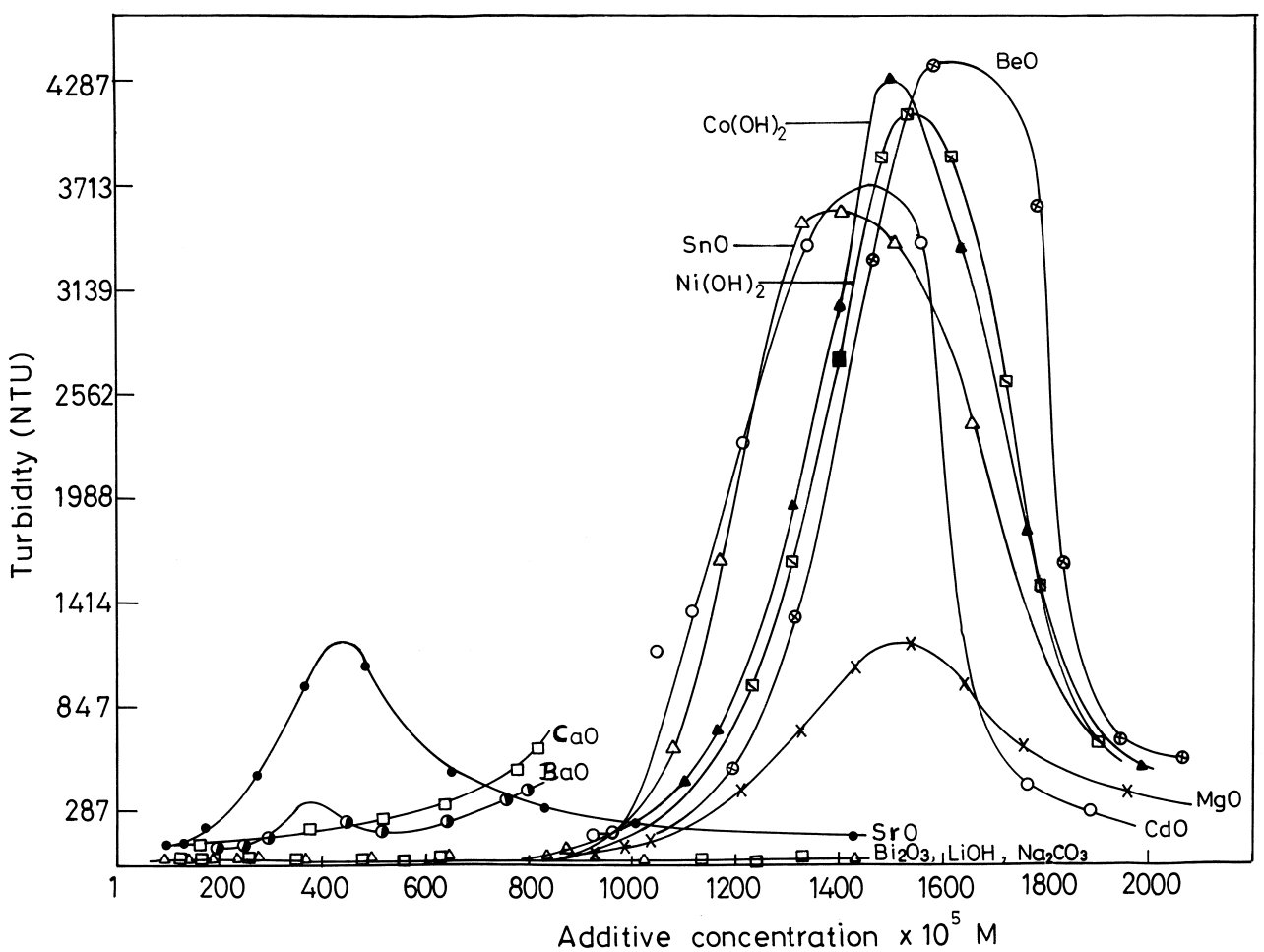

Fig. 7. Turbidity pattern of zincate (4 M NaOH) in presence of additives.

experimental techniques employed in this study, viz., IR and Raman spectra, cyclic voltammetry, and Hull cell analysis [20]. The unambiguousness of classification of the additives revealed by turbidity measurement is praiseworthy, in the sense that such a simple inexpensive technique can prove immensely useful in understanding the processes taking place in zincate solution. CdO, BeO, MgO, $Ni(OH)_2$, and $Co(OH)_2$ exhibit a bell-shaped curve in turbidimetry. This curve can be explained as follows. The five additives are known to form solid solutions with zinc oxide [31,32,40,43], and it is established now that coprecipitation and hydrolytic synthesis are excellent techniques for the preparation of solid solutions [28–30]. In the formation of a solid solution, molecular composition is an important factor. Other factors such as crystal lattice parameter being favourable, solid solution formation takes place only over the range of molecular composition of the individual entities. This range is represented by the peak region of the curve. On either side of the peak region, disproportionation occurs and the entities are present only as mixtures. In other words, formation of a solid solution is represented by an increase in particle size of the dispersed phase.

Group (ii) additives, viz., CaO, BaO, and SrO, are the alkaline earth oxides and have a common feature, i.e., all of them are capable of forming zincate compounds for example, calcium oxide forms calcium zincate, $Ca[Zn(OH)_3]_2 \cdot 2H_2O$ [11,43]; barium oxide forms at least two zincates, $Ba[Zn(OH)_4]$ and $Ba_2[Zn(OH)_6]$; and strontium oxide forms two zincates $Sr[Zn(OH)_4]H_2O$, $Sr_2Zn(OH)_6$ [44–47]. Cyclic voltammetry of a zinc electrode in the presence of these additives has, however, shown that BaO and SrO differ from CaO. This distinction may be attributed to some special properties of the former oxides. For instance, they can form solid solutions with

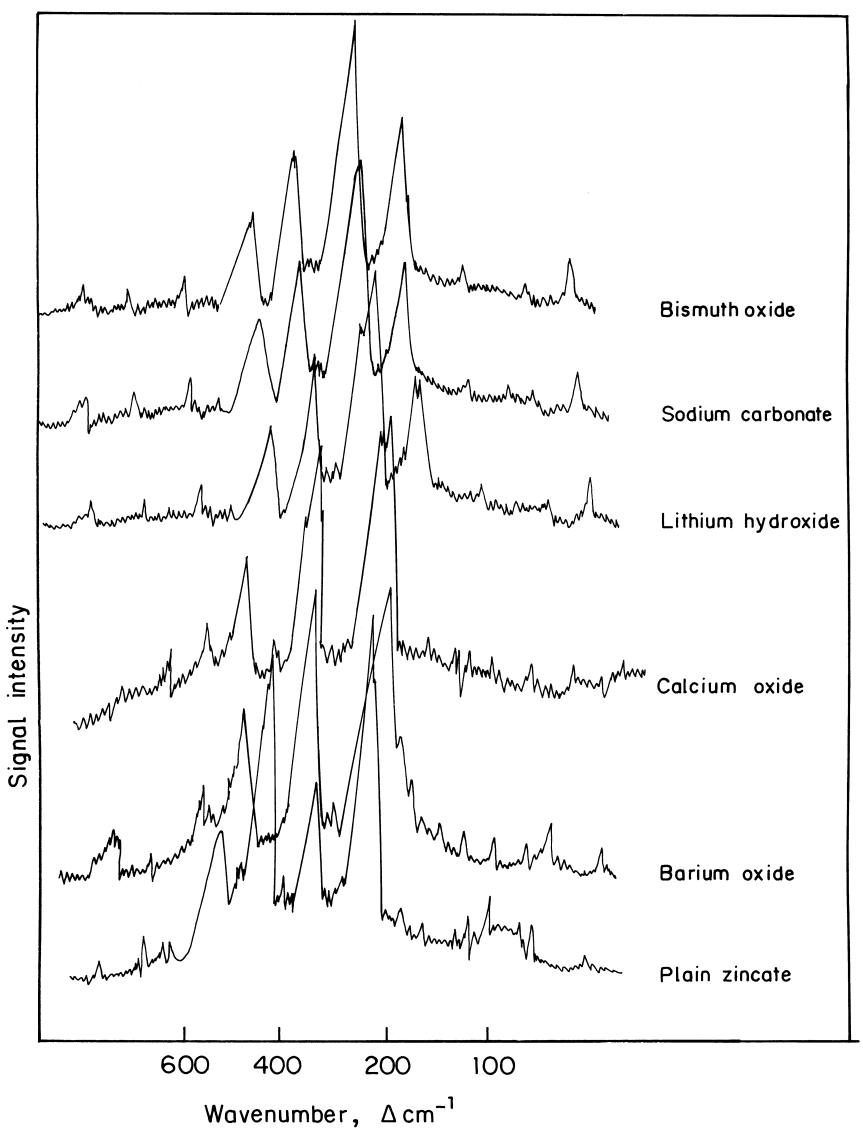

Fig. 8. Raman spectra of zincate with additive.

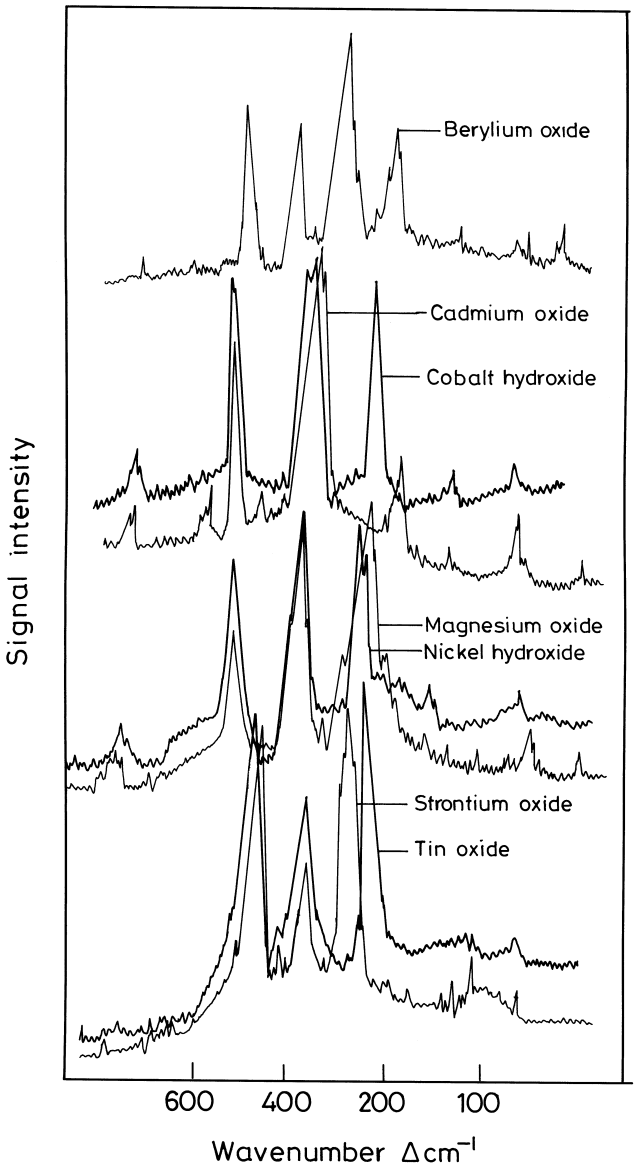

Fig. 9. Raman spectra of zincate with additive.

zinc oxide and other metal oxides [48–51] whereas CaO prefers to form only zincates. This difference in the chemical reactivity between CaO and BaO and of SrO is clearly revealed in the turbidity pattern. For BaO and SrO, there is a tendency towards a bell-shaped curve (although the particle size range is not as high as that of BeO and MgO), whereas this feature is absent for CaO.

Group (iii) additives are typified by their free solubility in zincate; Na_2CO_3 and LiOH, in particular, have exclusive solubility in zincate. Carbonate has been shown to form complexes with zincate [52] and at least two complexation modes have been indicated. The similarity in the turbidity spectrum of LiOH and Bi_2O_3 in zincate with that of carbonate indicates that the former additives enter into complexation with zincate.

In relevance to the complexation process proposed, Raman spectral analysis [20] has shown similarity in the binding features of Na_2CO_3 LiOH and Bi_2O_3 towards zincate. Cyclic voltammetric data of zinc/zinc oxide show higher dissolution current for these additives [12,42]. This means that all the three additives aid the dissolution of $ZnO/Zn(OH)_2$ and retain the same in solution [12–14,42,53]. It is also known that LiOH and K_2CO_3 stabilize supersaturated zincate [16,17,54]. A supersaturated zincate solution is thought to consist of three states [6,55], namely: (i) individual zincate ions; (ii) an unstable colloidal state involving zinc oxide/hydroxide; (iii) a relatively stable polymeric state. Additives like xylitol, molasses and citrate [6,56] stabilize a polymeric zincate structure. It has been proposed that hydrogen ions and zincate ions 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 the solution. It is reasonable to expect that like LiOH and Na_2CO_3, Bi_2O_3 also enters into complexation with zincate.

McBreen and Gannon [12] found Bi_2O_3 to be a good additive for the zinc electrode. Similarly, BeO and MgO incorporation into ZnO [43] improved the cycle-life of ZnO/NiOOH cells, both shape change and dendritic growth were absent in these cells. These observations re-emphasize that BeO, MgO, CdO, $Ni(OH)_2$, and $Co(OH)_2$ each provide a good host lattice for ZnO [25–27].

3.3. Raman spectral analysis

Zincate ion has four characteristic Raman absorptions at 550, 470, 350, and 225 Δ cm^{-1} [57]. These absorptions suffer marked shifts in the presence of the additives studied in the present work (Figs. 8 and 9). As can be seen from the Raman data (Table 2), LiOH, Na_2CO_3, and Bi_2O_3 as a class exhibit distinct behaviour in that all the

Table 2
Raman spectral features of zincate in presence of various additives

Additives	Raman frequency Δ cm^{-1}			
	A	B	C	D
Plain zincate	550	380	330	250
SrO	500	352		273
BaO	530	350		200
CaO	470	330		210
LiOH	430	350	240	175
Na_2CO_3	450	350	270	185
Bi_2O_3	460	380	280	190
MgO	545	359		220
CdO	545	320		210
BeO	480	380	270	170
SnO	480	354		228
$Ni(OH)_2$	545	359		258
$Co(OH)_2$	545	317		229

four absorptions of zincate are retained, although there is some shift. The shift is more or less of the same magnitude for LiOH and Na_2CO_3, whereas slightly higher values are observed for Bi_2O_3.

MgO, CdO, BeO, SnO, $Ni(OH)_2$, and $Co(OH)_2$ are seen to represent a class in the values of their frequency. BeO, however, also shows the fourth frequency.

In respect of the frequency values, BaO, SrO, and CaO can be grouped together. CaO, however, shows lower frequency values.

The classification of additives revealed by Raman spectral analysis is in agreement with the classification revealed by turbidimetry.

4. Conclusions

Techniques of turbidimetry and Raman spectral analysis have been employed in the present study to investigate the interaction of zincate with additives. Both techniques enable an identical classification of additives in terms of their action. An important conclusion that is drawn from the present study is that a simple inexpensive technique, viz., turbidimetry, can be employed to understand the solute behaviour of certain additives in zincate solutions. This is in line with the work of Debiemme and Vedal [58], who used nephelometry to investigate the kinetics of the zincate ageing process and the work from our laboratory [56] that employed turbidimetry to ascertain the micellization and complexation processes in zincate solution.

The present work has enabled an understanding of the chemical nature of the products formed when zinc dissolves electrochemically in 4 M NaOH.

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