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On The Use of Methylimidazolium Acetate Ionic Liquids as Solvent and Stabilizer in the Synthesis of Cobalt Nanoparticles by Chemical Reduction Method

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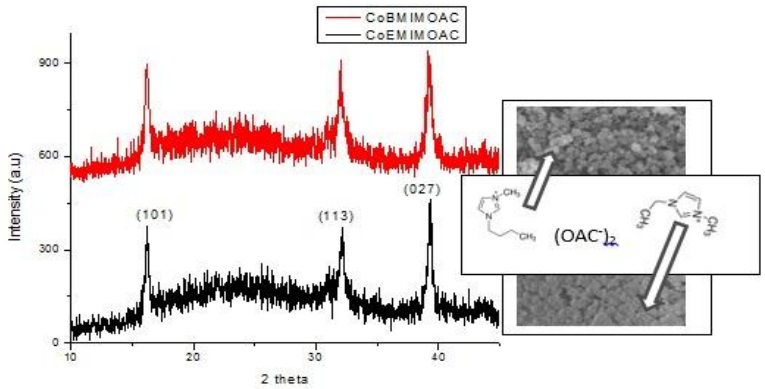
ABSTRACT

1-ethyl-3-methylimidazolium acetate (EMIMOAC) and 1-buthyl-3-methylimidazolium acetate (BMIMOAC) ionic liquids have been used as a solvent and stabilizing agent in an attempt to prepare cobalt nanoparticles via chemical reduction method. The SEM and UV-Vis techniques confirm the formation of nanoparticles. XRD reveals the Nano crystalline nature of the products with average crystallite size of 27.5 and 24.1 nm for CoEMIMOAC and CoBMIMOAC, respectively. The SEM and EDAX morphological/atomic weight ratio analyses do not show much difference between the Nano crystals formed in EMIMOAC or BMIMOAC. These results indicate that the cationic part of the ionic liquid did not play significant role during nucleation and growth of the particles. The inhibition zone diameter (IZD) shows moderate susceptibility against *Staphylococcus aureus* to CoBMIMOAC (15 mm) but high susceptibility to CoEMIMOAC with a larger inhibition zone diameter of 23 mm. Gram-negative microorganism *E. coli* is moderately susceptible to both CoEMIMOAC (14 mm), and CoBMIMOAC (15 mm).

GRAPHICAL ABSTRACT



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Introduction

The use of ionic liquids (ILs) in the synthesis of inorganic nanomaterials has received great attention [1-7], not only for being environmentally benign solvent, but also for ease of preparing complex inorganic materials that cannot be made using conventional solvents [8-11]. Ionic liquids (ILs) can stabilize metal and metal oxide nanoparticles through their high ionic charge, their polarity and high dielectric constants [12-16].

The physical size of materials can be used to tune materials properties. Properties such as optical, magnetic, and catalytic properties are quite interesting at the nanometer size regime with resultant applications in chemical technology, magnetic data storage, and sensing, *etc.* [17]. Efforts to explore structures on the nanometer length scale unite the frontiers of materials chemistry, physics, and engineering. It is in the design and characterization of advanced materials that the importance of new interdisciplinary studies may be realized. Uncovering and mapping size-dependent materials properties requires synthetic routes to prepare homologous size series of monodisperse nanometer size crystals, known as nanocrystals (NCs). NC samples must be monodisperse in terms of size, shape, internal structure, and surface chemistry [18]. In the study, ionic liquids based on 1-ethyl-3-methylimidazolium (EMIM) or 1-butyl-3-methylimidazolium (BMIM) cations and acetate anion have been used to prepare cobalt-based Nano crystals and their antibacterial properties evaluated.

Materials and methods

Materials

Cobalt (II) chloride hexahydrate ($CoCl_2.6H_2O$), Sodium tetrahydroborate (III) [$NaBH_4$], Sodium hydroxide, ionic liquid based on 1-ethyl-3-methylimidazolium (EMIM) and 1-buthyl-3-methylimidazolium (BMIM) cations and acetate anions (OAc) were obtained from commercial source and used as received.

Preparation of the Cobalt Nano crystals

Exactly 23.793 g of cobalt (II) chloride hexahydrate (assay = 99.9%) was dissolved in 50 cm^3 of ethylene glycol (ethane-1, 2-diol). A portion of this solution (8 cm^3) was dispersed in 3 cm^3 of 1-ethyl-3-methylimidazolium acetate (EMIMOAC)/or 1-buthyl-3-methylimidazolium acetate (BMIMOAC) under constant stirring at room temperature. The maroon-blue solution became black on addition of $NaBH_4$ (0.00945 g) and 1.5 cm^3 of 0.5 M NaOH with evolution of colourless fumes. The mixture was then heated to 70 °C within 3 h. The colloidal dispersion obtained was centrifuged and the

precipitate washed and dried at room temperature.

Antimicrobial Studies

Antimicrobial test was carried out in the Department of Microbiology, University of Calabar. The disc diffusion method was adopted [19]. With the help of a cotton swap, isolated colonies of the organisms were suspended in 5 cm^3 saline Mueller-Hilton. The turbidity of the suspension was matched with the turbidity standard (equivalent to a 0.5 McFarland standard). A discrete colony of each of the isolate was picked with a sterile wire loop and streaked on the Muller-Hilton agar plate. About 2000 µg of CoEMIMOAC, CoBMIMOAC and amoxicillin were transferred to the agar plates. Within 30 minutes of applying the disc, the plate was inverted and incubated aerobically at 35 °C for 18 h. At the end of incubation, zones of inhibition (ZOI) were measured and recorded in millimeters.

Characterization

The samples were analyzed by Rigaku MiniFlex II X-ray diffractometer using monochromatic Cu Kα radiation (λ = 0.1541 nm) at the speed of 3s in 2θ range between 5 - 750 and step size of 0.03.

The peaks were analyzed using the Scherrer formula [20]:

$$D_{hkl} = \frac{k\lambda}{\beta(\frac{\pi}{180})cos\theta}$$

Where D_{hkl} is the coherence length of the crystalline domain perpendicular to the respective *hkl* plane, k is a constant (here 0.9), λ is the wavelength of CuKα radiation (1.5406 Å), β is the background corrected line broadening in degrees, (π/180) is a correction factor to calculate β in radians, and θ is the scattering angle. The scanning electron microscopy (SEM) studies of the nanocrystals were made with a Field Emission Electron Microscope (FESEM JSM-6700 F), coupled with an energy dispersion analyzer (EDX). The specimens were Au coated (sputtering) to make them conductive. The SEM acceleration voltage was 10 kV. The Fourier transform infrared (FTIR) spectra for the synthesized Nano crystals were recorded over the wave number range of 400-4000 cm^{-1} using Perkin Elmer FTIR spectrometer. The powdered samples were mixed with KBr (in a 1: 200 ratio of their weight) and pressed in the form of pellets for measurement. Ultraviolet/Visible Spectroscopic measurements were carried out using 201 Evolution UV-Visible spectrophotometer. A portion (1 cm^3) of methanolic solution of the precipitates (0.1 g of solid dissolved in 5 cm^3 of methanol) was taken out and dispersed in 5 cm^3 of distilled water for the UV-Vis measurement.

Results and discussion

Nano crystals have been synthesized *via*

chemical reduction of the cobalt chloride hexahydrate by NaBH4 in ILs EMIMOAC / or BMIMOAC. The reactions were performed at elevated temperatures to obtain homogeneous reaction mixtures. The colour changes from maroon blue to black.

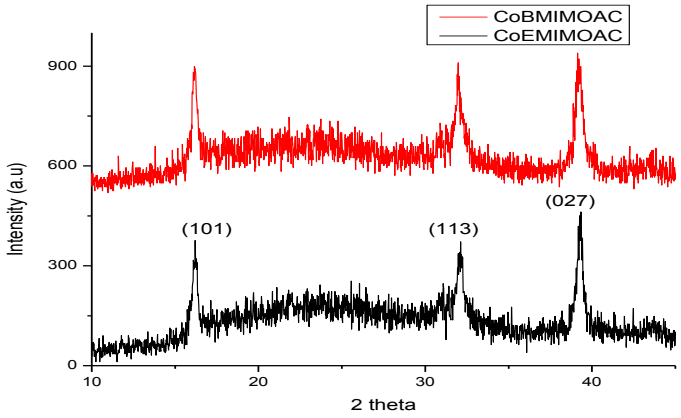

Figure 1. Powder X-ray diffraction pattern of the nanocrystals

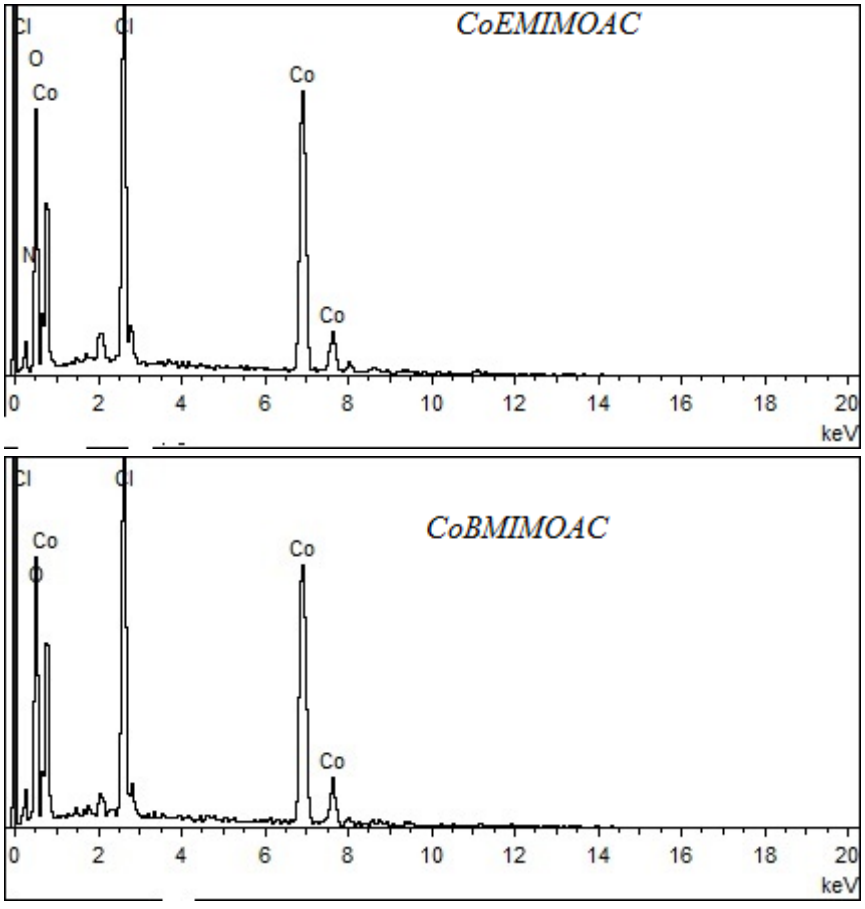

Figure 2. EDAX spectra of as-synthesized cobalt nanocrystals grown in imidazolium-based ILs

Figure 1 shows a typical X-ray diffraction (XRD) pattern of the nanocrystals formed after isolation and drying. XRD identifies the products to be Cobalt hydroxide chloride (Ref. code = 01-073-2134, ISCD = 24685). The most representative reflections of $Co_2(OH)_3Cl$ were indexed in rhombohedral crystal space group R-3m (No.166) with the following unit cell dimensions : a = b = 6.8400 Å , c = 14.500 Å, α = β= 90°, γ = 120° , Vol. =587.50 Å^3 , Z =6. The representative reflections of (101), (113), and (024) were observed at 2θ values of 16.2, 32.12 and 39.26°, respectively with corresponding interplanar distances of $d_{101} = 5.4837, d_{113} = 2.7918\ and\ d_{024} =$ 2.2936 Å. The average crystallite size D_{hkl} (coherence lengths) calculated using Scherrer equation [19] is 27.5 nm for CoEMIMOAC and 24.1 nm for CoBMIMOAC. For the XRD pattern shown in Figure 1, the D_{101} is 29.13, D_{113} is 26.26, D_{024} is 35.72, and D_{027} is 18.85 nm.

Figure 2 shows the energy dispersive analysis by X-ray (EDAX), while Figure 3 gives representative scanning electron microscopy (SEM) images of the products. The EDAX results for sample grown in EMIMOAC ionic liquid showed the percentage of cobalt, chlorine, oxygen and nitrogen to be 50.66, 16.19, 31.51 and 1.64 %, respectively. Whereas the percentage of cobalt, chlorine and oxygen is 49.16, 17.25 and 33.59%, respectively for sample grown in BMIMOAC. The SEM reveals a monodisperse Nano crystals in both EMIMOAC and BMIMOAC.

Figure 4 shows the UV-Vis spectrum of sample grown in EMIMOAC. The spectrum exhibit well-defined absorption bands which can be assigned to the surface Plasmon absorption of the Nano crystals. The surface Plasmon resonance can be thought of as the coherent motion of the conduction-band electrons caused by interaction with an electromagnetic field. The frequency and width of the surface Plasmon absorption depend on the size and shape of the metal nanoparticle as well as on the dielectric constant of the metal itself and of the medium surrounding it [21–23]. It can be seen in Figure 4 that the surface Plasmon resonance splits into two bands, with the higher energy band in the range 430-460 nm and the lower energy in the region 500 -560 nm.

FTIR spectrum of the Nano crystals grown in either EMIMOAC or BMIMOAC ionic liquid (Figure 5) showed broad absorption band centered around 3447 cm^{-1}, which can be attributed to the N-H stretching vibration. The bands at 1504 and 1410 cm^{-1} can be assigned to C=C vibrations of the imidazolium ring indicating that the ionic liquids have been adsorbed on the surface of the nanocrystals thus providing electrosteric stabilization of the particles in agreement with literature reports [24-30]. The bands in the region 656-426 cm^{-1} are attributed to Co-O vibrations.

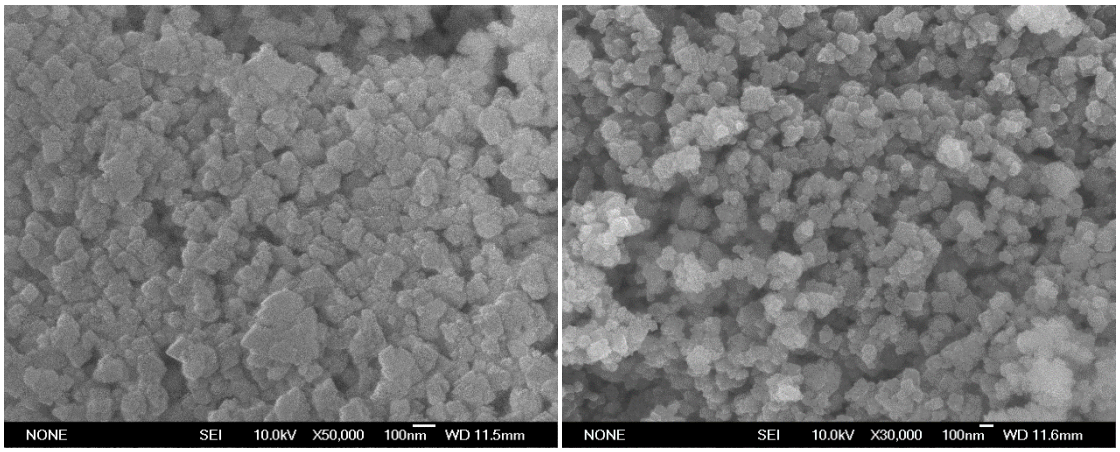

Figure 3. Representative SEM images of particles grown in (a) EMIMOAC (b) BMIMOAC

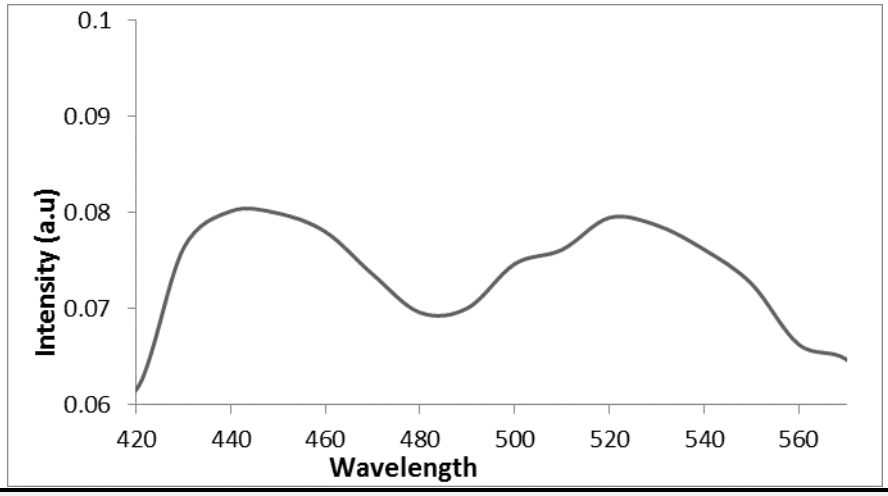

Figure 4. UV-Visible spectrum of cobalt nanoparticles in IL EMIMOAC

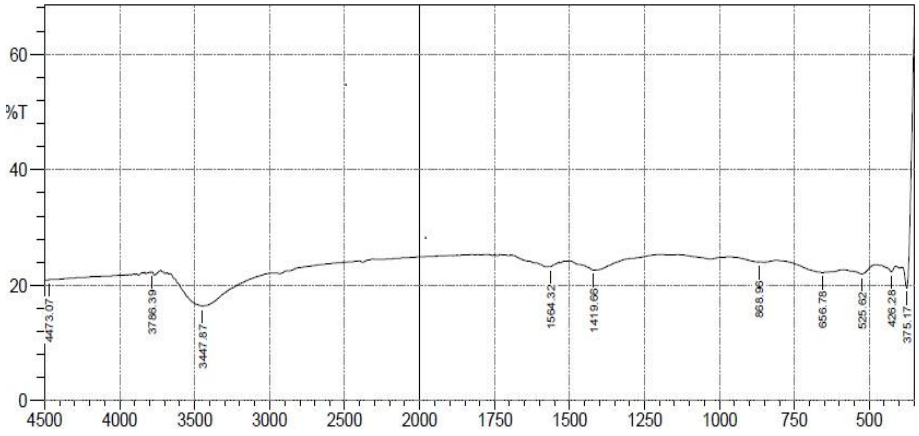

Figure 5. FTIR spectrum of particles grown in EMIMOAC

The potential of the synthesized Nano crystals to inhibit the bacterial growth was evaluated and comparison made to the over the counter drug amoxicillin as shown in Table 1, Figure 6. The inhibition zone diameter (IZD) shows moderate susceptibility against *Staphylococcus aureus* to CoBMIMOAC (15 mm) but high susceptibility to CoEMIMOAC with a larger inhibition zone diameter of 23 mm. Gram-negative microorganism *E. coli* is moderately susceptible to both CoEMIMOAC (14 mm), and CoBMIMOAC (15 mm). The inhibition zone diameter of CoEMIMOAC show high susceptibility to *Staphylococcus aureus* and moderately susceptible to *E. coli* suggesting its high susceptibility to gram-positive microorganism than gram-negative (*E. coli*). The Nano drug: CoEMIMOAC performs better than amoxicillin in inhibiting of *Staphylococcus aureus*.

Table 1. Zones of inhibition (ZOI) of bacterial growth by the synthesized nanocrystals

	CoEMIMOAC	**CoBMIMOAC**	**Amoxicillin**
	ZOI	ZOI	ZOI
Staphylococcus aureus	23 mm	15 mm	14 mm
Escherichia coli	14 mm	15 mm	20 mm

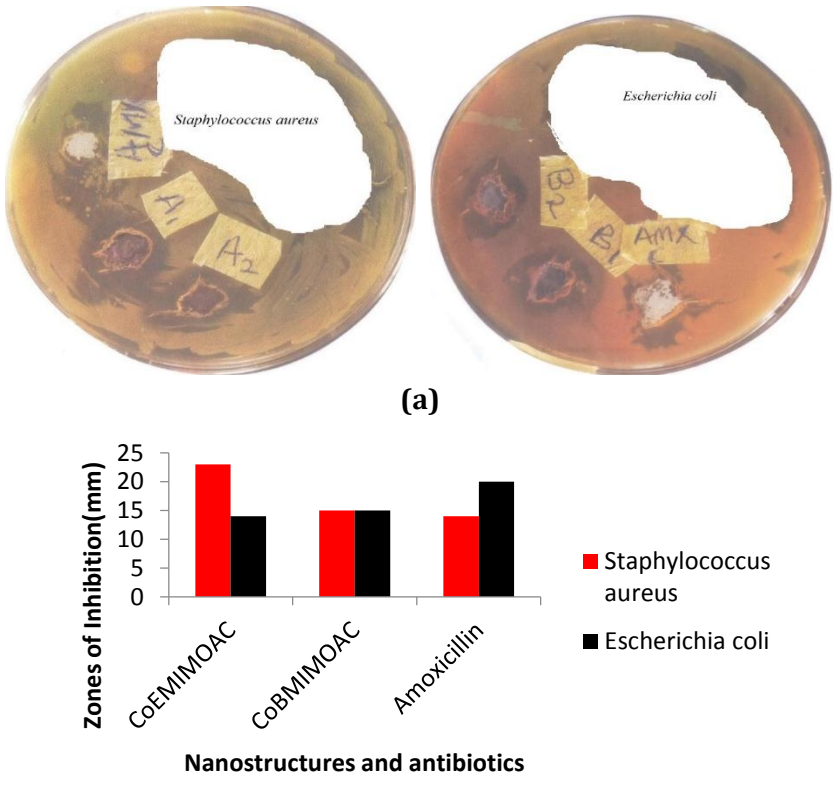

Figure 6. (a) Agar plates showing zones of inhibition. *Staphylococcus aureus:* CoEMIMOAC = A_1 and CoBMIMOAC = A_2 ; *Escherichia coli*: CoEMIMOAC = B_1 and CoBMIMOAC = B_2, Amoxicillin = AMX (b) Bar chart showing inhibition zone diameter

Conclusion

In conclusion, 1-ethyl-3-methylimidazolium acetate (EMIMOAC)/or 1-buthyl-3-methylimidazolium acetate (BMIMOAC) ionic liquids have been successfully used as a solvent and stabilizer in the synthesis of Nano crystals of cobalt. The SEM and UV-Vis techniques confirm the formation of nanoparticles. XRD revealed the Nano crystalline nature of the products. There was no difference between the Nano crystals formed in EMIMOAC or BMIMOAC indicating that the cationic part of the ionic liquid did not play significant role during nucleation and growth of the particles. The zone of inhibition of CoEMIMOAC obtained against *S. aureus and E. coli* are 23 and 14 mm, respectively whereas that of CoBMIMOAC against the two bacterial under investigation is 15 mm. The synthesized Nano crystals have therefore demonstrated great potentials as Nano drugs in the treatment of infections caused by gram-positive microorganisms.

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