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Synthesis of Calcium Oxalate Particles Using Emulsion Liquid Membrane (ELM): Effect of Molar Ratio (Ca/OA) on Particle Morphology

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Abstract: ***There are three hydrate forms of Calcium oxalate which are crystallized in different morphologies and the natural occurrence is connected with the three minerals whewellite as (COM) monoclinic monohydrate, (COD) weddilite as orthorhombic dehydrate and (COT) caoxite as triclinic trihydrate. Emulsion Liquid Membrane (ELM) systems is a useful tool for quick and selective removal of metals from dilute aqueous streams. Calcium oxalate used as filler and a pigment in coated paper and the cardboard industry to impart brightness.***

Keywords: Calcium Oxalate, COM, COD, COT, Concentration Precursor, ELM, molar ratio

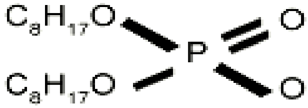
1. Introduction

There are three hydrate forms of Calcium oxalate which are crystallized in different morphologies and the natural occurrence is connected with the three minerals whewellite as monoclinic monohydrate (COM), weddilite as orthorhombic dehydrate (COD) and caoxite as triclinic trihydrate. Of the three hydrates (COM, COD, COT) only the monohydrate form is thermodynamically stable. The dihydrate and trihydrate are not stable and when left in contact with the supernatant liquid get transformed to COM. Calcium oxalate also has a commercial importance; it is used as filler and a pigment in coated paper and the cardboard industry to impart brightness.

Literature indicates that many parameters like precipitation time, stirring, presence of inhibitors and surfactants affect the calcium oxalate hydrate forms and their morphology.

2. Reagents for Synthesis of Calcium Oxalate Particles

1) *Calcium Salts:* Calcium Nitrate Tetra hydrate (minimum assay 99%) of AR grade supplied by S. D. fine chem. Ltd., Calcium Chloride dihydrates (minimum assay 97%) of AR grade supplied by Merck specialties private Ltd., was used as a precursor to synthesis the particles.
2) *Oxalic Acid:* AR grade with a minimum assay 99.8% from S.D. fine chem. Ltd. was used to precipitate the oxalate salt from their respective precursors.
3) *Sorbitane Monooleate (Span 80):* Span 80, nonionic surfactant used for the preparation of W/O emulsion was of S. D. fine chem. Ltd. make with saponification value of 145-160, hydroxyl value of 190-215, water content <1.0%, acid value < 8.0 and density of 0.9944 g/cc.
4) *Extractant:* D2EHPA (di-(2ethylhexyl) phosphoric Acid) ($C_{16}H_{35}PO_4$) having structural formula as shown below and a boiling point of 48 ºC at 12 mm Hg, flash point 137 ºC and density 0.97 g/cc supplied by FLUKA Chemicals Private limited was used as extractant.



5) *Kerosene:* Kerosene having boiling point range 152-271 ^{0}C with viscosity of 1.6 cP and specific gravity 0.8 at 30 ^{0}C, supplied by Indian Oil Corporation Limited Vadodara was used as the oil phase for preparation the emulsion.
6) *Sodium Hydroxide:* Sodium hydroxide pellets of AR grade with minimum assay 98.0% from S.D. fine chem. Ltd. were used to prepare NaOH of different molarities and adjust the pH of external aqueous phase.
7) *Buffer solutions:* Buffer tablets of pH 4.0 and pH 7.0 from Merck Specialties Private Ltd were used to calibrate digital pH meter.
8) Acetone and ethanol (AR grade from Merck specialties private Limited), were used to demulsify the emulsion and wash the synthesized particles.

3. Synthesis of Calcium Oxalate Particles

Precipitation using facilitated transport in confined spaces (Emulsion Liquid Membranes):
The precipitation reaction for formation of calcium oxalate proceeds via a simple ionic double decomposition reaction.

$$Ca(NO_3)_2 4H_2O + H_2C_2O_{4(aq)} \longrightarrow CaC_2O_4xH_2O_{(s)} + 2\ HNO_{3\ (aq)}$$

3.1 Preparation of calcium oxalate particles in ELMs

The experimental set up consisted of a glass baffled reactor (4 baffles) of 9.82 cm I.D. and 14.0 cm height equipped with a six bladed turbine agitator assembly. The agitator was driven by a fractional HP (1/8) variable speed motor (REMI make 0.95 Amp, with 12 HP, 220-230 V). A rheostat from MAGGSTAT ELECTRICALS was provided to control the input voltage to the motor driven the agitator, so that the speed could be maintained constant. The dimensional specification of the assembly is shown in Figure 3.2.1.

600 ml of feed solution (initial calcium concentration 500 mg/L (7.537 x 10^{-3} moles) was contacted with 100 ml of the cured emulsion at 160 rpm and 30 ± 2 ^{0}C so, as to give a treat ratio of 1:6. After 30 min of mixing, the W/O emulsion was separated from the external feed solution and demulsified by adding definite amount of acetone/ethanol. The particles, formed in the internal phase of emulsion, were then separated by centrifuging at 5000 rpm, washed with acetone/ethanol, and dried.

Precipitation in ELMs is based on the principal of facilitated transport II wherein the alkali metal ions bind with a suitable extractant to get transported through the oil phase membrane to the internal phase membrane interface to get precipitated in the internal droplets of the emulsion containing the precipitating agent.

In comparison to homogeneous precipitation which is instantaneous there is a time gap for precipitation in ELMs. The precursor is in the bulk phase which is the stirred phase has to get transported to the internal phase and the particles are precipitated in the internal droplets which are stagnant droplets. This behavior is identical to precipitation in homogeneous quiescent media. There is no restriction in homogeneous phase but there is phase and transport restriction in ELMs.

Synthesis of particles is an ELM offers a distinct advantage of producing particles of controlled sizes. The size selectivity of an ELM is obtained because precipitation takes place within the internal droplets of a W/O emulsion. Under normal emulsification conditions the internal drop size in an emulsion range from 1-10 µm with an average size of ~3 µm. Hence, the particles synthesized within an ELM would yield sizes < 3 µm.

Before carrying out precipitation in an ELM the mechanism needs to be developed wherein the Ca^{+2} ions can be transported and precipitated in the internal phase droplets. Since cation transport necessitates the addition of an extractant in the oil membrane phase which would selectively bind the cation at the external oil- water interphase. Ca ion transfer into ELM follows facilitated type – II mechanisms.

$$2RH + Ca^{2+} \leftrightarrow R_2Ca + 2H^+ \text{ --------------------------- } (1)$$

$$R_2Ca + 2H^+ \leftrightarrow 2RH + Ca^{2+} \text{ --------------------------- } (2)$$

The internal phase reaction (2) will free the extractant and strip the Ca ions from the extractant and seed the particle making the extractant free to bind more cations to be transported to external phase. In this system D2EHPA was used as the extractant due to its commercial availability. It can be seen that D2EHPA extracts calcium at wide range of pH values from 1.5 to 2.8. The pH of the feed was maintained at 6.

3.2 Effect of molar ratio (Ca/OA) on particle morphology

Initially the M.R. of Ca/OA was varied by keeping the Ca concentration at (0.0125 M) and varying the oxalic acid concentration. The CaOx particles obtained were characterized using SEM, XRD, FT-IR shows the XRD spectra obtained at three molar ratios of 0.5, 1.0 and 2.0 respectively. It can be seen that as molar ratio increased i.e. acid concentrations decreased, the crystallite size also decreased.

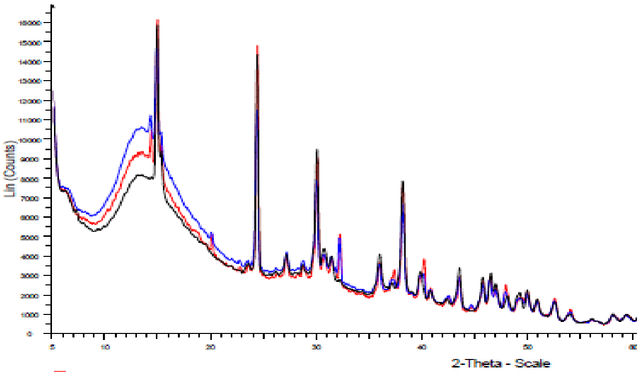


Figure 3.2.1: Comparison of XRD spectra for CaOx particles synthesized in ELMs at varying molar ratios.
[▬ M.R. = 0.5 ▬ M.R. = 1.0 ▬ M.R. = 2.0]

Table 4.4 (a) shows the d-spacing of the major three peaks for the hydromorphs and the scherrer values at varying M.R.s.

Table 3.2.2 (b): Standard d- spacing.

	d1	d2	d3	d4
COM	5.97	3.64	2.98	5.77
COD	6.18	4.42	2.77	2.24
COT	2.84	5.52	5.48	4.99

When the M.R. = 0.5, 72.7% COM, 10.6% COT and 16.7% anhydrous CaOx was observed. Fig. 4.15 shows the SEM particles of the synthesized CaOx. It can be seen that majority of these hydrates are of COM twins with size = 182.9 nm. Since the oxalic acid concentration was high it is expected that COM twins would grow. The presence of COT along with COM is confirmed from the FT-IR spectra (Fig. 3.2.3). Table 3.2.2 (a) shows the IR bands associated with the various groups.

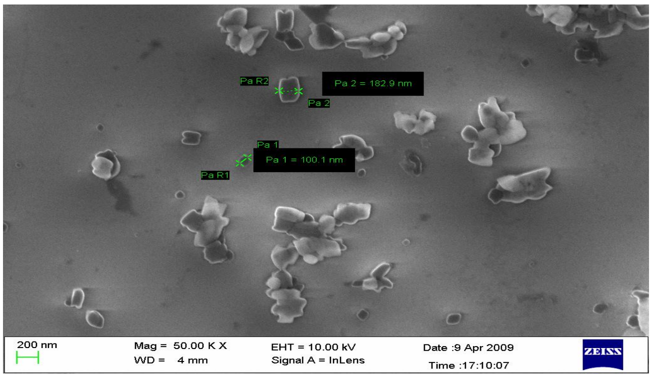


Figure 3.2.3: SEM picture of calcium oxalate monohydrate twins at Ca/OA molar ratio 0.5 in ELM

Table 3.2.2 (a): XRD comparison for ELM: 0.15 M calcium nitrate, time 30 min

Precursor Concentration (M)	Oxalic acid Concetration (M)	Φ	M.R.	Extractant (v/v)	Hydrates obtained	Crystallize Size (scherrer)	Measured d-spacing			
							d1	d2	d3	d4
0.0125	0.3	0.5	0.5	10%	72.7% COM (M) 10.6% COT (T) CaOx 16.7%	304.8 A 85.6 A 175.1 A	5.95	3.65	2.97	2.355
0.0125	0.15	0.5	1	10%	54.7% COM, 23.1% COD (T) CaOx 22.2%	360 A 82.8 A 81.4 A	5.94	3.65	2.97	2.352
0.0125	0.075	0.5	2	10%	69.1% COM, 30.9% CaOx	259.8 A 81.4 A	5.96	3.65	6.198	2.97
0.0125	0.3	0.64	0.5	10%	59.8% COM, 18.5% COT (T), 21.7% CaOx	226.3 A 90.5 A 90.4 A	5.918	3.639	2.965	2.355
0.0125	0.3	0.5	0.5	1%	63.2 % COM (T) 20.4% COT 16.4% CaOx	133.5 A 82.5 A 100.6 A	5.93	3.649	2.969	2.355
0.0125 (2 hrs)	0.3	0.5	0.5	10%	65.8% COM (M) 9.0% COD (T) 25.1% CaOx	335.1 A 82.9 A 88.0 A	5.917	3.638	2.965	6.55
0.004	0.048	0.5	1.0	10%	69.8% COM, 30.2% CaOx	289.5 A 82.6 A	5.947	3.648	2.973	2.355
0.0125 (CaCl2)	0.3	0.5	1.0	10%	70% COM, 30% CaOx	262.4 A 83.4A	5.889	3.627	2.958	2.347

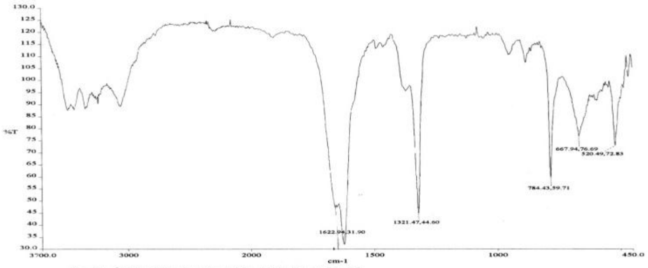


Figure 3.2.3: FT-IR spectra of calcium oxalate particles synthesized by ELM at M.R. = 0.5

Antisymmetric carbonate stretching band [Vas (COO^-)/cm^1] specific to oxalate family, for COT occurs as double peaks at 1670/1617 cm^{-1} these are observed at 1670/1622 cm^{-1}. The secondary carbonyl stretching band the metal carboxylate located at 1317 cm^{-1} shifted to 1321.4 cm^{-1}.

In the finger print region, very sharp peak at 784 cm^{-1} attested the presence of COM and characteristic peak at 667 cm^{-1} and 520.49 cm^{-1} indicate that COT crystals do grow.

Experiments were also conducted by increasing the contact time of emulsion and feed from 30 min. to 2 hours under identical conditions. It was observed that (Table 3.2.2 (a))

COT disappeared and 9.0% COD was obtained. It is well known that COT is a thermodynamically unstable state which eventually gets converted to metastable COD and later to thermodynamically stable COM. Fig. 3.2.4 shows the SEM pictures where presence of COM is justified.

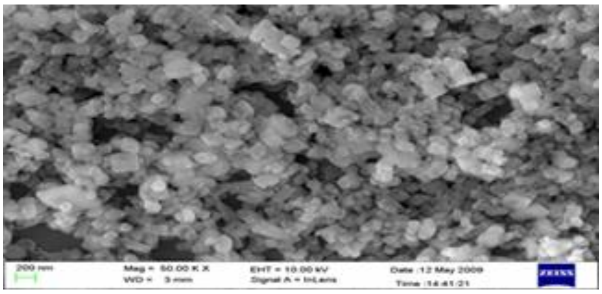


Figure 3.2.4: SEM picture of calcium oxalate monohydrate twins at Ca/OA molar ratio 0.5 and precipitation time 2 hrs in ELM

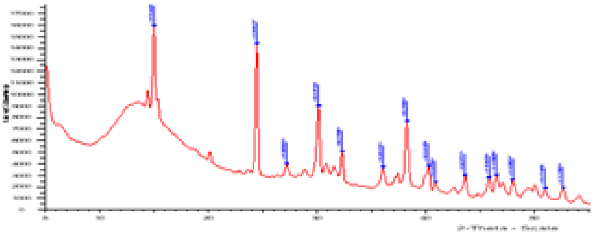


Figure 3.2.5: XRD spectra of calcium oxalate for particles synthesized at Ca/OA molar ratio 1.0 in ELM

Increasing the M.R. from 0.5 to 1.0 resulted in a decrease in COM from 72.7% at M.R. = 0.5 to 54.7% at M.R. = 1.0, 23.1% COD was obtained. Fig. 3.2.5 shows the XRD plots at Ca/OA M.R. = 1.0. It can be seen from the SEM pictures (Fig. 3.2.6) COM and COD both morphologies are present. Diamond shape morphology for COM is obtained. Whereas envelop shaped COD are present. Sizes of the COD particles were (500nm-1µm) in comparison to that of COM (500 nm).

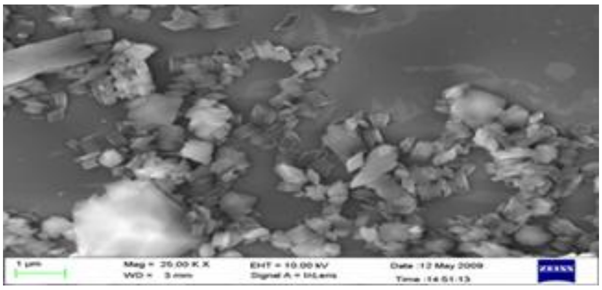


Figure 3.2.6: SEM picture of calcium oxalate at Ca/OA molar ratio 1.0 and precipitation in ELM

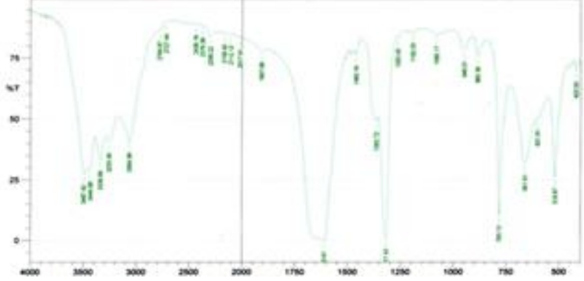


Figure 3.2.7: FT-IR spectra of calcium oxalate particles synthesized by ELM at M.R. = 1.0

The FT-IR plot however did not show a peak at 1648 cm^{-1} indicative of COD. The peak for presence of COM was detected at 1610 cm^{-1}(Fig.3.2.7).

Further increasing the M.R. = 2.0, all of the COT and COD got converted and 69.1% COM was obtained along with 30.9% CaOx anhydrous.

In all the three molar ratio variations CaOx anhydrous was obtained. Hirai et al (2004) reported that the internal phase droplets are always water deficit, this may have led to the presence of anhydrous CaOx. It was felt that if precipitation took place in a greater volume, probably the anhydrous from may not be present. In view of this the internal phase volume fraction was increased from 0.5 to 0.64 at MR = 2. This is the maximum amount of initial phase that can be added to a W/O emulsion so that increasing the volume fraction of the internal phase increased the internal phase droplet sizes from 3.364 μm at $\Phi = 0.5$ to 4.84 μm at $\Phi = 0.64$ with the precipitation taking place in a greater volume of water. It was observed that 72% COM and 27.4% COT was obtained (Table 3.2.2 (a)) and no anhydrous CaOx was obtained. This itself justifies that in all the earlier cases the precipitation took place in water deficit environments. If under these conditions if the emulsions were cured for a greater period of time after contact 100% COM could have been obtained.

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Author Profile

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