Synthesis of Calcium Oxalate Particles in Confined Spaces: Emulsion Liquid Membrane (ELM)

Harsh Bharatkumar Shukla

Chemical Engineering Department, Shri K J Polytechnic, Bharuch, Gujarat, India
Email: *shuklahb22[at]gmail.com*

Abstract: ***Calcium oxalate (CaOx), a biomineral occurs in both plant and the animal kingdom. 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. Emulsion liquid membrane process is achieved by preparing an emulsion between two immiscible phases and then dispersing the emulsion formed into a third (continuous) phase by agitation so as to extract a solute from the continuous phase into the inner phase of the emulsion or vice-versa. The membrane phase is the liquid that separates the encapsulated internal droplets within the emulsion from the external continuous phase. 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

1. Introduction

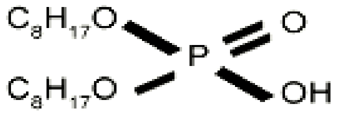
Calcium oxalate (CaOx), a biomineral occurs in both plant and the animal kingdom. Calcium oxalate is the most abundant mineral present in the human kidney stones and is therefore widely studied by urologists in an effort to understand the onset of the disease and prevent kidney stones.

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 relative super saturation, pH, 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.

$$Ca(NO_3)_2 4H_2O + H_2C_2O_{4(aq)} \longrightarrow CaC_2O_4 x H_2O_{(s)} + 2\ HNO_{3\ (aq)}$$

Emulsion Liquid Membrane (ELM) systems is a useful tool for quick and selective removal of metals from dilute aqueous streams. Emulsion liquid membrane process is achieved by preparing an emulsion between two immiscible phases and then dispersing the emulsion formed into a third (continuous) phase by agitation so as to extract a solute from the continuous phase into the inner phase of the emulsion or vice-versa (Fig. 3.1.1). The membrane phase is the liquid that separates the encapsulated internal droplets within the emulsion from the external continuous phase (Fig. 3.1.2).

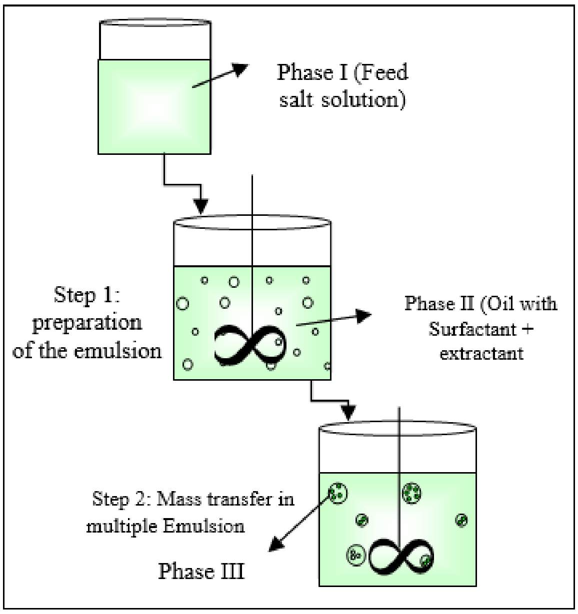


Figure 3.1.1: Preparation of Emulsion Liquid Membrane

The liquid membrane usually contains surfactants, additives, and a base material, which is a solvent for all other gradients. The surfactants and additives are used to control the stability, permeability, and selectivity of membrane. The constituents of ELM for extraction of solute must be chosen in such a way that once the solute diffuses into the inner receiving phase, it cannot diffuse back into the continuous phase.

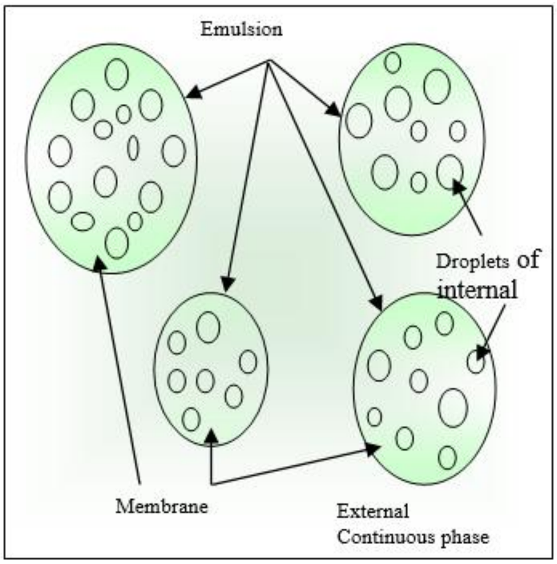


Figure 3.1.2: Schematic of an Emulsion Liquid Membrane System

When the emulsion is dispersed by mild agitation in a continuous phase, many small globules (0.1-3 mm in diameter) of the emulsion are formed. These globules are stable and do not disintegrate, when the system agitated. The size of the globules is mainly dependent on the type of surfactant, emulsion viscosity, and mode and intensity of mixing. Each emulsion globule contains many encapsulated droplets of 1 µm in diameter. Large number of globules can easily produce correspondingly large membrane surface area for rapid mass transfer.

A large surface area for mass transfer is generated because of the small size of emulsion globules formed. The internal encapsulated droplets (Fig.31.2) within the globule are at 1 – 10 µm in diameter thereby generating an enormously large internal mass transfer area of the order of 10^{6} m^2/m^3 resulting in rapid mass transfer rates.

Once separation is achieved the emulsion is separated from the continuous phase by settling. Demulsification of emulsion can help to recover the solute. In this manner solute could be removed from large volume of the bulk phase and get concentrated within the internal phase of the emulsion.

There are two types of facilitation mechanisms in an ELM system. Type I facilitation uses a reactive agent in the internal phase of the emulsion to irreversibly react with the solute and form a product incapable of diffusing back through the membrane and encapsulating the product. Since diffusing solutes are soluble in membrane phase selectivity and separation depends solely on the partition coefficient of the solute. Typical example of type I transport are the extraction of week acids (phenols, acetates) where the internal phase contains an stripping base (Fig 3.1.3a) and extraction of week bases (ammonia, amines) where internal phase contains an acid.

In type II facilitation, the solute is incapable of diffusing on its own through the membrane phase. Hence, a carrier is incorporated in membrane phase to enhance the rate of transport. The carrier not only facilitates mass transfer but also enhances the separation selectivity (Fig.3.1.3 b).

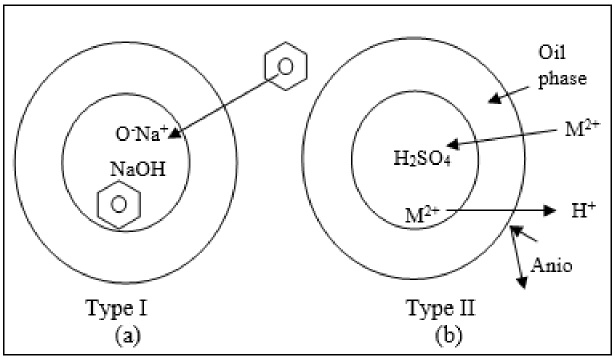


Figure 3.1.3: Facilitated Mechanisms in ELMs

The main area of application of type II facilitation is in the extraction cations from aqueous solutions. The association of solute with the carrier / extractant generates an extractant ion complex which is highly soluble in the organic membrane phase. The extractant shuttles the metal ion within the emulsion membrane globule.

The internal phase of the emulsion contains an appropriate stripping agent to carry out the stripping reaction at the membrane-internal phase interphase. The metal ion gets released in the internal phase rendering the extractant free to shuttle more metal ions in the internal phase. This process continues as long as the stripping phase gets exhausted. For e.g. a bivalent metal ion (M^{2+}) reacts with the ion exchange reagent (RH) present in the membrane phase as a carrier at the external surface of the emulsion globules according to reaction (1).

$2RH + M^{2+} \leftrightarrow R_2M + 2H^+$ -------------------------- (1)

The complex R_2M diffuses through the membrane to the inner aqueous phase where the metal ion gets stripped from the carrier according to reaction (2).

$R_2M + 2H^+ \leftrightarrow 2RH + M^{2+}$ -------------------------- (2)

The liberated carrier now shuttles to scavenge more metal ions while the stripped metal ions are effectively encapsulated in internal phase of the membrane.

Type II facilitation is used to extract cations from aqueous streams (Fig.3.1.4).

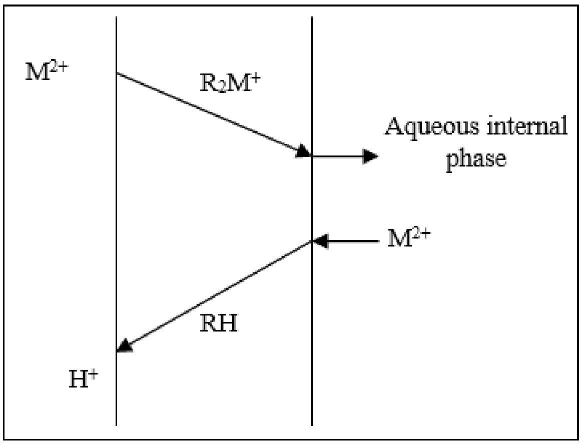


Figure 3.1.4: Mass transfer in facilitated transport II

ELM system is capable of being used as a "micro reactor" for the preparation of size-controlled and morphology-controlled fine particles due to the confined reaction area of the internal water droplets. This micro reactor is also interesting because it provides a hydrophobic environment and templating effect at the interface between the organic membrane phase and internal water phase. In addition, purification and pre-concentration of the target metals are not needed since the ELM system could have very high selectivity for the specific metal depending on the extractant used.

The internal phase of the emulsion can also be used to precipitate calcium to its corresponding oxalate when the strippant is oxalic acid. The consumption of calcium by precipitation as the oxalate causes further stripping from the organic membrane phase and hence enhanced extraction (Reaction 3).

$Ca^{2+} + (COOH)_2 \leftrightarrow Ca\,(COO)_2 \downarrow + 2H^+$ ---------------- (3)

1) Emulsion preparation for extraction of calcium ions:

Membrane (emulsion) was prepared in a 600ml glass beaker of 7.632 cm I.D. and 15.0 cm height. The membrane phase was prepared by dissolving 5% (w/v) span 80 and 1-10% v/v extractant (D2EHPA) in (47-42.5 ml) kerosene. Equal volume of strippant (oxalic acid, 0.1-0.3 M) and the membrane phase were blended at 12000 rpm for 6 minutes to obtain milky white emulsion. Emulsions prepared were cured for 30 minutes prior to characterization and making measurements.

2) Emulsion Characterization:

a) *Internal drop size measurement:*

Internal droplet sizes of the emulsion were observed under an OLYMPUS microscope (model BHS) equipped with a PM-10AD Olympus photo micrographic system. Emulsions were diluted with kerosene (1:45) and the diluted emulsions were mounted on a slide and covered with a 0.5 mm thick cover slip.

Droplet sizes were measured at 600x magnification using an ocular micrometer (graduated scale) (Erma make) and a stage micrometer, a 3"x1" glass slide on which a millimeter scale is imprinted, graduation of this scale is in hundredths of millimeter. The measurement of drop sizes by this method required the calibration of the ocular micrometer with the stage device. The value of single ocular meter unit (O) was calculated as,

$$O = \frac{\text{Distance of 10 stage divisions (mm)}}{\text{Number of eyepiece divisions}}$$
$$= \frac{0.1}{30} = 3.33\ \mu m$$

On calibrating the ocular, the stage micrometer was removed and the prepared slide was placed. Once the slide was focused, the number of division (N) covered by the droplet was counted and size of the droplet was calculated by multiplying the number of division (N) with the calculated value of O that is 3.33 μm.

b) *Viscosity Measurement:*

Emulsion viscosity was measured using a Brookfield cone and plate rheometer, LVDV- Ⅲ using CPE-52(cone angle 3 degree, and radius 1.2) at varying shear rates.

3) 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 3.1.5.

600 ml of feed solution (initial calcium concentration 500 mg/L (7.537×10^{-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.

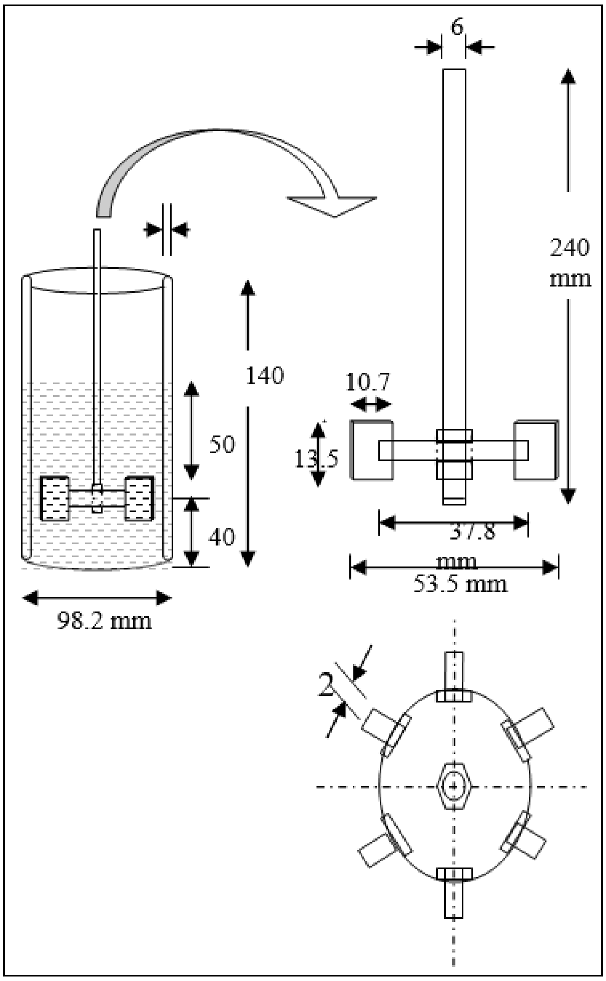


Figure 3.1.5: Dimensional assembly of agitator vessel

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Author Profile

Harsh Shukla received the B.E. and M.E. degrees in Chemical Engineering from SVMIT and M.S. University in 2006 and 2009, respectively. After 2010, I am working as a Lecturer in Chemical Engineering Department in Shri K J Polytechnic, Bharuch