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SHORT COMMUNICATION

Crystallization and Dissolution Behavior of L(+) Calcium and Zinc Lactate in Ethanol-Water Solvent

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Abstract−Crystallization and dissolution behavior of L(+) calcium and zinc lactate in 50% ethanol-water solution was studied. The effects of stirring, standing, ultrasonic wave, and temperature on the crystallization of L(+) calcium and zinc lactate were evaluated. It was found that standing had a positive effect on crystallization of L(+) calcium and zinc lactate, while stirring promoted dissolution of crystallized particles and resulted in high residual concentration in mother liquor. The application of ultrasonic wave did not influence much on crystallization process. L(+) calcium and zinc lactate crystallized easily at 5 °C; however, complete crystallization took more than 72 hours. These two salts dissolved rapidly and reached equilibrium within 1 hour.

Key words: L(+) Calcium Lactate, L(+) Zinc Lactate, Crystallization, Dissolution

INTRODUCTION

Calcium and zinc lactate are important chemicals of the lactic acid industry, widely used as nutrients in food and medicine for lack of calcium and zinc [Chen et al., 1995; Xue et al., 1993; Yang et al., 1998; Zhang et al., 1994]. Zinc lactate is also used as an ingredient of toothpaste, cosmetics, oral composition, sex drugs [Keooy et al., 1997; Shah et al., 1984; Vlock et al., 1992] and polymerization of polylactide [Kricheldorf et al., 1997, 1998; Schwach et al., 1998]. It is a key chemical in the drug, food, health, and chemical industries.

Recently, L(+) lactic acid has been emphasized as it is utilized by the human body and its polymer is biodegradable. The value of lactates has also been noticed in the food and pharmaceutical industries. However, not much data regarding crystallization of L(+) calcium and zinc lactate have been reported in the literature. Recently, the solubility of calcium and zinc lactates in water and ethanol-water was reported [Cao et al., 2001]. In 50% (w/w) ethanol-water solvent, calcium and zinc lactates showed low solubility. However, it is possible to crystallize calcium and zinc lactates from their ethanol-water solution with high recovery. In this study, crystallization and dissolution behaviour of calcium and zinc lactate in 50% water-ethanol solvent was investigated. The results can be used in preparation of L(+) calcium and zinc lactate solutions, and also in the development of recovery process of L(+) lactic acid in the fermentation industry.

EXPERIMENTAL

1. Materials

L(+) calcium lactate [$Ca(CH_3CHOHCOO)_2 \cdot 2H_2O$] and L(+) zinc lactate [$Zn(CH_3CHOHCOO)_2 \cdot H_2O$] were purchased from Sigma Chemical Company. Conductivity of solution was measured by a conductivity meter (H19032 Hanna, Singapore) connected to a computer. Temperature was controlled by a digital temperature controller (PolyScience, U.S.A.) and ultrasonification was carried out by a vibrio and cell ultrasonic instrument (Sonics & Material Inc., U.S.A.).

2. Assay Method

Concentration of L(+) calcium and zinc lactate was measured by using a conductivity meter. A linear calibration curve was obtained between a salt concentration and conductivity up to 2% (w/w).

3. Effect of Stirring on Crystallization of L(+) Calcium and Zinc Lactates

Two aliquots of L(+) calcium lactate were prepared by dissolving 3.5 g L(+) calcium lactate (3 gram as anhydrous salt) in 48.25 g of water, followed by the addition of 48.25 g ethanol. The solution was cooled down to 5 °C. One aliquot was stirred at 200 rpm and the other was let stand without stir at 5 °C. After centrifugation, 1 g supernatant was taken out from crystallization suspension intermittently and dried at 60 °C to evaporate ethanol. The residual was dissolved in water to make the solution 10 g. The conductivity of supernatant was measured to determine the lactate concentrations as the amount of anhydrous salt in 100 g solution.

Two aliquots of L(+) zinc lactate were prepared by dissolving 2.5 g L(+) zinc lactate (2.34 gram as anhydrous salt) in 48.75 g water and then 48.75 g ethanol was added. The following steps were the same as the L(+) calcium lactate experiment.

4. Effect of Ultrasonic wave on Crystallization

L(+) zinc lactate ethanol-water solution (2.24%) was prepared by dissolving 1.2 g of L(+) zinc lactate (1.12 gram as anhydrous salt) in 24.4 g of water and adding 24.40 g of ethanol to the solution. The solution was cooled down to 5 °C. Ultrasonic wave of 120 Watt was applied to the solution with 3 seconds and off for 1 second, and this cycle was repeated for 3 hours.

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5. Crystallization of L(+) Calcium and Zinc Lactate at 5 °C and 22 °C

Two aliquots of 2.93% of L(+) calcium lactate ethanol-water solution were prepared by dissolving 3.4 g of L(+) calcium lactate (2.93 gram as anhydrous salt) in 48.3 g water and adding 48.3 g ethanol to the solution. One aliquot was stood without stir at 22 °C and the other aliquot was left at 5 °C.

Two aliquots of 2.33% of L(+) zinc lactate ethanol-water solution were prepared by dissolving 2.5 g of L(+) zinc lactate (2.33 gram as anhydrous salt) in 48.75 g of water and adding 48.75 g ethanol to the solution. Following steps were the same as the L(+) calcium lactate experiment.

6. Dissolution of L(+) Calcium and Zinc Lactate in Ethanol-water

Twenty four grams of water and equal amount of ethanol were mixed together and cooled down to 5 °C and 2 g L(+) calcium lactate was added. The solution was stirred at 200 rpm. One gram of supernatant was taken out from suspension at different time and concentration was determined by the conductivity meter.

For L(+) zinc lactate experiment, 24.5 g water and equal amount of ethanol were mixed and cooled down to 5 °C and then 1.0 g L(+) zinc lactate was added. Following experimental conditions and steps were the same as L(+) calcium lactate experiments.

RESULTS AND DISCUSSION

1. Effect of Stirring on Crystallization of L(+) Calcium and Zinc Lactate

The change in concentration of L(+) calcium lactate and L(+) zinc lactate in supernatant with time is shown in Figs. 1 and 2, respectively. When the solution was stirred, L(+) calcium lactate concentration decreased rapidly at first, then increased slightly after 25 hours. After 48 hours L(+) calcium lactate concentration did not change much (ca. 1.94%) until 72 hours. However, the final concentration was different from the solubility of L(+) calcium lactate [Cao et al., 2001]. Probably stirring promoted dissolution of crystallized particles and inhibited crystallization of calcium lactate from the supersaturated solution. These processes were dominant compared to the aggregation of small particles. Consequently, equilibrium was maintained at a high residual concentration.

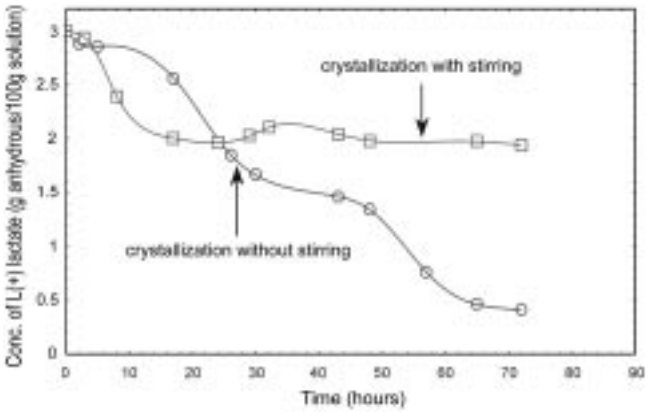

Fig. 1. Crystallization of L(+) calcium lactate in ethanol-water solution at 5 °C.

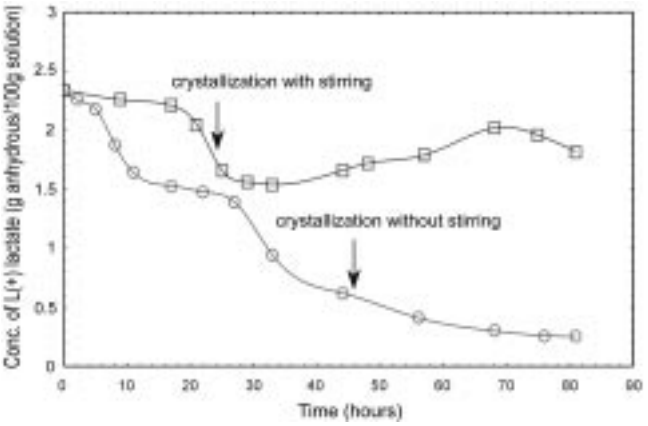

Fig. 2. Crystallization of L(+) zinc lactate in ethanol-water solution at 5 °C.

When the solution was not stirred, decrease in the concentration of L(+) calcium lactate was slightly delayed. After 72 hours, the concentration of L(+) calcium lactate in supernatant was 0.41%. This shows that standing without stir has a positive effect on the crystallization of L(+) calcium lactate. The crystallization process of smaller particles progressed slowly with aggregation into larger particles and higher level of crystallization was obtained.

For L(+) zinc lactate, stirring delayed crystallization and resulted in increase in the concentration of lactate in supernatant (Fig. 2). The situation was different from the crystallization of L(+) calcium lactate. Probably the differences in hydrated form and crystalline structure between calcium lactate and zinc lactate resulted in the difference in crystal development process under the same stirring condition. It is not clear why the concentration in supernatant slightly increased during the later crystallization. However, the re-dissolution rate of zinc lactate crystal might be higher than the crystallization rate of zinc lactate crystal. A different kinetic equilibrium was found to exist during crystallization under stirring condition. The crystallization behavior of L(+) zinc lactate was similar to L(+) calcium lactate without stirring. The final concentration of L(+) zinc lactate in supernatant was 0.25 % at 81 hours (Fig. 2).

2. Effect of Ultrasonic Wave on Crystallization of L(+) Zinc Lactate

Ultrasonification reduced induction time for the crystallization of DL(±) calcium lactate to one-sixth or one-eighth of that for the

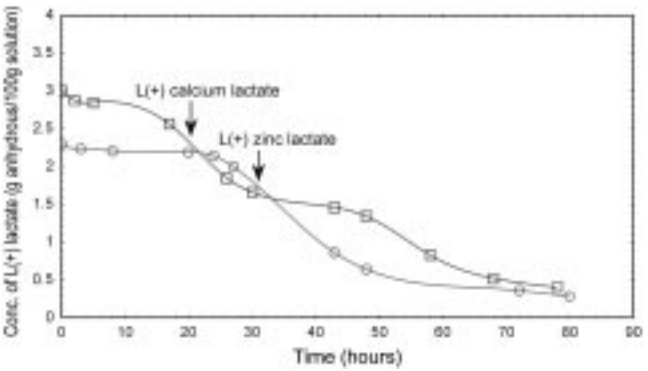

Fig. 3. Effect of ultrasonic wave on crystallization of L(+) calcium and zinc lactates.

crystallization without ultrasonification [Jin et al., 1994]. Ultrasonic wave was applied for the induction of L(+) calcium and zinc lactate crystallization. However, there was not any significant difference (Fig. 3). The concentration in supernatant decreased slightly after 3 hours of ultrasonic wave application. After 75 hours the concentration of L(+) calcium and zinc lactate was 0.40% and 0.28%, respectively. Overall crystallization time was not shortened. Variations in sonication intensity, application time, and application period were tried; however, similar results were obtained.

3. Crystallization of L(+) Calcium and Zinc Lactate at Different Temperatures

Crystallization of L(+) calcium and zinc lactate at 5 °C and 22 °C is shown in Figs. 4 and 5, respectively. At 22 °C, it was difficult to crystallize L(+) calcium lactate. Its concentration in supernatant decreased slowly with time and reached 1.08% after 75 hours. At 5 °C, more L(+) calcium lactate was crystallized. The concentration in supernatant was 0.41% after 72 hours.

At 22 °C, the concentration of L(+) zinc lactate in supernatant decreased slowly and was 0.82% at 72 hours. At 5 °C, it decreased more rapidly and was 0.25% at 75 hours. Higher crystallization yield was obtained at lower temperature. However, more energy is required to maintain the temperature below room temperature. Consequently, the crystallization yield and the energy consumption should be considered comprehensively. Variation in the sequence of solvent addition was not found to be significant for crystallization. When ethanol and lactate containing water were mixed together, the crystal did not appear for several hours. There was not any difference in crystallization process whether lactate containing water solution was added to ethanol or ethanol was added into lactate containing water solution.

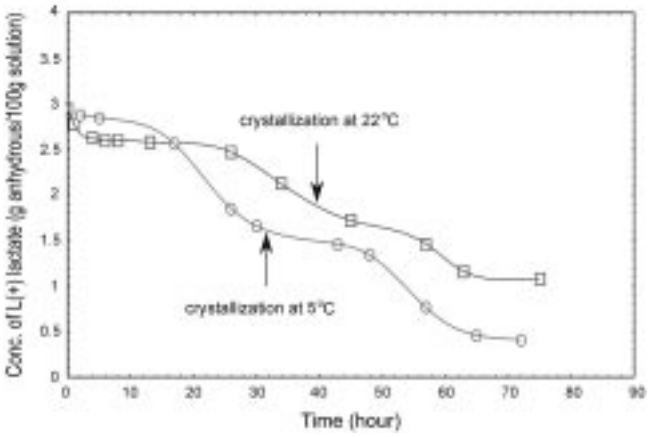

Fig. 4. Crystallization of L(+) calcium lactate without stirring at 5 °C and 22 °C.

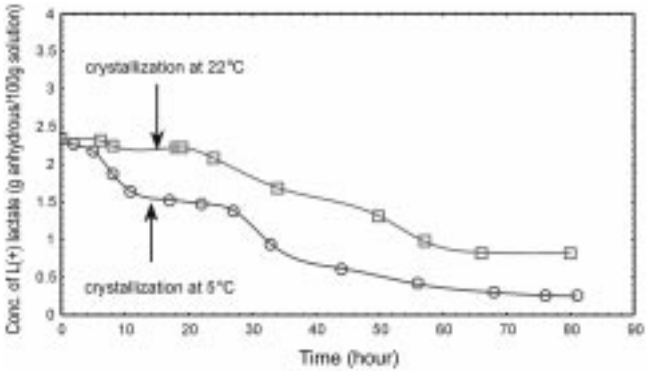

Fig. 5. Crystallization of L(+) zinc lactate without stirring at 5 °C and 22 °C.

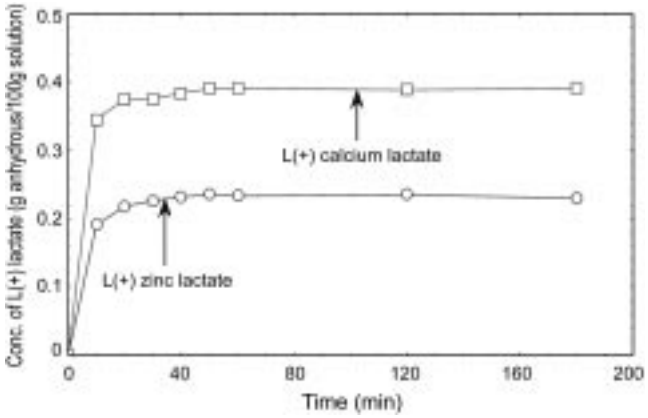

Fig. 6. Dissolution behavior of L(+) calcium and zinc lactate in ethanol-water solution.

4. Dissolution Rate of L(+) Calcium and Zinc Lactate

Dissolution behavior of L(+) calcium and zinc lactate with time is shown in Fig. 6. Both calcium and zinc lactate dissolved rapidly at first and reached equilibrium in 1 hour. The dissolution rate was much higher than the crystallization rate. Calcium lactate showed higher solubility than zinc lactate. The solubility of L(+) calcium and zinc lactate was 0.39% and 0.23%, respectively, at equilibrium. Dissolution of L(+) calcium and zinc lactate is a relatively simple process compared with the crystallization process that is affected by many factors.

CONCLUSIONS

L(+) calcium and zinc lactates were crystallized from 50% ethanol-water solution at 5 °C without stir after 48 hours. Stirring could promote re-dissolution of crystallized particles and result in a high residual concentration in the mother liquor. Application of ultrasonic wave did not significantly influence the crystallization of L(+) calcium and zinc lactates. Both L(+) calcium and zinc lactates were dissolved rapidly and reached equilibrium within 1 hour.

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