Korean J. Chem. Eng., **18**(1), 133-135 (2001)
SHORT COMMUNICATION

Solubilities of Calcium and Zinc Lactate in Water and Water-Ethanol Mixture

Xuejun Cao*, Ho-Joon Lee, Hyun Shik Yun and Yoon-Mo Koo†

*State Key Laboratory of Bioreactor Engineering, Department of Biochemical Engineering,
East China University of Science and Technology, Shanghai, 200237, China
Department of Biological Engineering, Inha University, 253 Yonghyundong, Namku, Inchon, 402-751, Korea
(*Received 21 August 2000 • accepted 26 December 2000*)

Abstract−The solubility of lactate salts, L(+) and DL(±) forms of calcium and zinc lactate in water at temperature between 5 and 80 °C, was measured and empirical equations were obtained by regression of solubility-temperature data. The equations can be used to calculate the solubility of calcium and zinc lactate at a given temperature. The change in solubility of L(+) and DL(±) calcium and zinc lactate in water-ethanol mixture at 20 °C was also investigated. The solubilities of calcium and zinc lactate were lowered by the addition of ethanol to the solution.

Key words: Solubility, Calcium Lactate, Zinc Lactate

INTRODUCTION

Calcium and zinc lactates are important chemicals in the lactic acid industry, and calcium lactate crystallization is a popular commercial separation method of lactic acid. Calcium and zinc salts of lactic acid are 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 for the manufacture of toothpaste, cosmetics, oral composition, sex drugs [Keooy et al., 1997; Shah et al., 1984; Vlock, 1992] and polymerization of polylactide [Kricheldorf et al., 1997, 1998; Schwach et al., 1998]. It is a potential chemical in drugs, food, health and chemical industry.

Recently L(+) lactic acid has drawn attention as it can be utilized by the human body and the polymer of L(+) lactic acid is biodegradable. However, little solubility data of calcium and zinc lactate have been reported in literature. In this study, the solubilities of calcium and zinc lactate in water and water-ethanol mixture were obtained experimentally. The solubility data can be used not only in the preparation of calcium and zinc lactate, but also in the recovery process of L(+) lactic acid in the fermentation industry.

EXPERIMENTAL

1. Materials

L(+) calcium lactate ($Ca(CH_3CHOHCOO)_2 \cdot 2H_2O$), DL(±) calcium lactate ($Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$), L(+) zinc lactate ($ZnCH_3CHOHCOO)_2 \cdot H_2O$), and DL(±) zinc lactate ($ZnCH_3CHOHCOO)_2 \cdot 3H_2O$) were of analytical grade and purchased from Sigma Chemical Co. Temperature was controlled by digital temperature controller (PolyScience, USA) and conductivity was measured by microcomputer conductivity meter (H19032 Hanna, Singapore).

2. Solubilities of Calcium and Zinc Lactate in Water

Various concentrations of calcium lactate and zinc lactate suspensions were prepared and stirred for 2 to 4 hours until they reached an equilibrium at a given temperature. The attainment of equilibrium was checked by measuring the concentration of samples every 30 min. Salts were added until they formed precipitates. Tested temperature range was between 5 and 80 °C with 5 °C intervals. If necessary, a short temperature interval was applied. One gram of supernatant was taken out from the suspension after equilibrium had been reached and was diluted 10 or 20 times with distilled water. Conductivity of each sample was measured and solubility was determined by conductivity-solubility calibration curve. The conductivity of the lactate solutions ranged from 5 to 4,000 μS as the concentration of lactate solution changed from 0.1 to 1.0% (w/w). Solubility was expressed by the amount of anhydrous salt dissolved in 100 g solution.

3. Solubilities of Calcium and Zinc Lactate in Water-Ethanol Mixture

Six aliquots of 0.5 g of L(+) calcium lactate, L(+) zinc lactate, DL(±) calcium lactate, and DL(±) zinc lactate were dissolved in 10 g water-ethanol solution (0, 10, 20, 30, 40 and 50% (w/w)), respectively. They were shaken for 48 hours at 20 °C and centrifuged at 8,000 rpm for 5 min. The supernatants were removed and undissolved solids were dried for 24 hours at 60 °C to evaporate ethanol. The dried solids were redissolved in water. Each sample solution was prepared at 10 g and its conductivity was measured. The solubility was calculated from the total amount of solid added by subtracting the amount of undissolved solid.

RESULTS AND DISCUSSION

1. Solubilities of Calcium and Zinc Lactate in Water

The solubilities of L(+) and DL(±) calcium lactate at temperatures between 5 and 80 °C are shown in Fig. 1. The solubilities of both salts increased gradually with temperature below 50 °C, but increased rapidly with temperature above 50 °C. L(+) calcium lactate showed higher solubility than DL(±) calcium lactate in water. At 80 °C, the solubility of L(+) calcium lactate was 45.88% (w/w, g anhydrous salt in 100 g solution), while the solubility of DL(±) calcium lactate was 36.48% (w/w).

The solubilities of L(+) and DL(±) zinc lactates in water at a tem-

†To whom correspondence should be addressed.
E-mail: ymkoo@inha.ac.kr

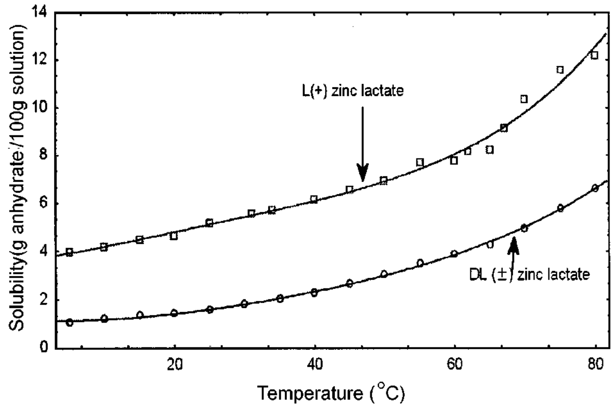

Fig. 1. Effect of temperature on solubility of L(+) and DL(±) calcium lactates.

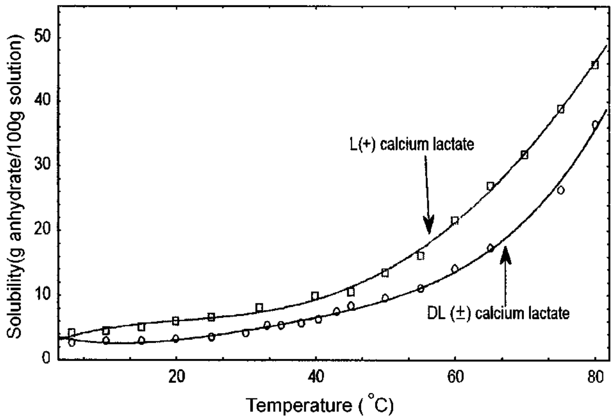

Fig. 2. Effect of temperature on solubility of L(+) and DL(±) zinc lactates.

perature range between 5 and 80 °C are shown in Fig. 2. L(+) zinc lactate showed higher solubility than DL(±) zinc lactate. At 10 °C, the solubility of L(+) zinc lactate was 4.22% while it was 12.16% at 80 °C. When the temperature increased from 5 to 65 °C, the solubility increased slowly with temperature. However, it increased rapidly at a temperature between 65 and 80 °C. DL (±) zinc lactate showed lower solubility than L(+) zinc lactate. At 10 °C, the solubility of DL (±) zinc lactate was only 1.21% and it was 6.62% at 80 °C.

L(+) and D(−) zinc lactates have almost same the solubility; however, D(−) and L(+) zinc lactates have higher solubilities than DL(±) zinc lactate [Pederson et al., 1926]. This is probably due to the different interaction among zinc lactates in racemic DL(±) zinc lactate solution. The D(−)-L(+) interaction is probably different from D(−)-D(−) or L(+)-L(+) interactions; moreover, different hydration degree of lactates in L(+), D(−) and DL(±) zinc lactate solution could result in the difference in the solubility. It has been reported that DL(±) calcium lactate crystallized below 41 °C contains five molecular hydrates while DL(±) calcium lactate crystallized above 41 °C contains three molecular hydrates in therm-weight analysis [Xie et al., 1991]. This indicates that the change in the degree of hydration could result in the change in solubility. L(+) and DL(±) zinc lactates showed lower solubility than calcium lactates. This may due to the higher molecular weight of zinc ion, which is expected to bind lactates more easily to be precipitated from the solution.

The relation of solubility to temperature shown in Fig. 1 and Fig. 2 was regressed. The regression equations, which were obtained for four lactate salts and are shown in Table 1, are expressed by 4th order polynomial equations and can fit the experimental data well. They can be used to calculate the solubility of calcium and zinc lactate at a given temperature.

2. Solubilities of Calcium and Zinc Lactate in Water-Ethanol Mixture

Calcium and zinc lactate are highly soluble in water; consequently, it is necessary to reduce their solubility to separate them from the solution. The change in solubility of L(+) calcium lactate and DL(±) calcium lactate with ethanol concentration at 20 °C is shown in Fig. 3. The solubility of L(+) calcium lactate decreased more rapidly with ethanol concentration. At 50% (w/w) ethanol concentration, the solubility of L(+) calcium lactate was 1.03%, while that of DL(±) calcium lactate was 1.49%. The two curves cross at approximately 43% ethanol concentration, which means that L(+) and

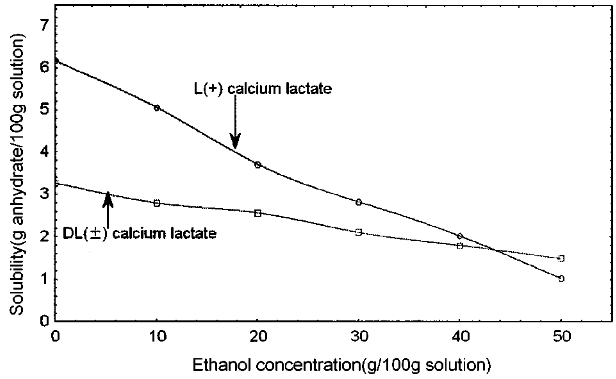

Fig. 3. Effect of ethanol concentration of L(+) and DL(±) calcium lactates (temperature: 20 °C).

Table 1. Regression equations for the solubilities of calcium and zinc lactate

Chemicals	Equations
DL(±) calcium lactate	$S=4.53-0.37T+0.02T^2-4.24\times10^{-4}T^3+3.31\times10^{-6}T^4$
L(+) calcium lactate	$S=1.93+0.45T-0.019T^2+3.51\times10^{-4}T^3-1.28\times10^{-6}T^4$
DL(±) zinc lactate	$S=1.15-0.012T+0.00168T^2-2.3\times10^{-5}T^3+1.83\times10^{-7}T^4$
L(+) zinc lactate	$S=3.7+0.0412T+0.0013T^2-3.56\times10^{-5}T^3+3.78\times10^{-7}T^4$

S: solubility (g anhydrate/100 g solution).
T: temperature (5-80 °C).

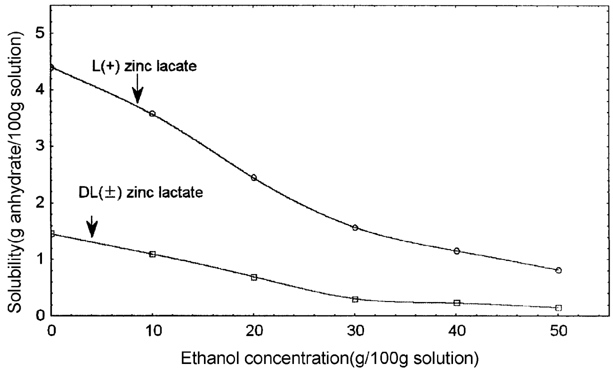

Fig. 4. Effect of ethanol concentration of L(+) and DL(±) zinc lactates (temperature: 20 °C).

DL(±) have the same solubility at the ethanol concentration.

The solubilities of L(+) and DL(±) zinc lactates in relation to ethanol concentration are shown in Fig. 4. They decreased with ethanol concentration at 20 °C, while they decreased more rapidly at ethanol concentration between 30 and 50%. L(+) zinc lactate showed higher solubility than DL(±) zinc lactate. The solubility of L(+) zinc lactate was 3.57% at 10% ethanol and 0.82% at 50% ethanol concentration, while the solubility of DL(±) zinc lactate was 1.1% at 10% ethanol concentration and 0.15% at 50% ethanol concentration.

The solubility of four lactate salts decreased with ethanol concentration. L(+) calcium lactate showed the highest solubility among them, secondly L(+) zinc lactate, and followed by DL(±) calcium lactate and DL(±) zinc lactate. L(+) salt showed higher solubility than its DL(±) mixture. When lactate salts are dissolved in water, it is necessary to add ethanol to the water solution to decrease the solubility. The liquid-liquid equilibria for alcohol-water-lactates systems will be studied by referring to some publications [Joung et al., 1998; Munthukumaran et al., 1999].

CONCLUSIONS

Calcium and zinc lactates are important products of the lactic acid industry and the solubility is one of their important physical properties. Solubilities of L(+) and DL(±) forms of calcium and zinc lactate in water at temperature between 5 and 80 °C and their solubility in water-ethanol mixture (up to 50% (w/w) ethanol) at 20 °C were obtained. Empirical equations that correlate the solubility of lactate salts in water were also presented. The results provide a useful reference for the recovery of lactic acid in the lactic acid fermentation industry.

ACKNOWLEDGEMENTS

This research work was supported by the Project Development for the Clean Production Technology of the Korean Ministry of Commerce, Industry and Energy, and the Project of Brain Korea 21.

REFERENCES

Chen, B., Lu, Z. T. and Huang, Z. D., "Production of L-calcium Lactate from Corp Powder by Direct Fermentation," *J. Huaqiao Univ.* (*Natural Science*), **16**(3), 318 (1995).

Joung, S. N., Shin, H. Y., Park, Y. H. and Yoo, K.-P., "Measurement and Correlation of Solubility of Disperse Anthraquinone and Azo Dyes in Supercritical Carbon Dioxide," *Korean J. Chem. Eng.*, **15**, 78 (1998).

Keooy, P. D., US patent, **5**, 599551 (1997).

Kricheldorf, H. R. and Damrau, D. O., "Polymerizations of L-Lactide Initiated with Zn(II) L-lactate and Other Resorbable Zn Salts," *Macromol. Chem. Phys.*, **198**, 1753 (1997).

Kricheldorf, H. R. and Damrau, D. O., "Zn L-lactate-catalyzed Polymerizations of 1,4-Dioxan-2-one," *Macromol. Chem. Phys.*, **199**, 1089 (1998).

Munthukumaran, P., Gupta, R. B., Sung, H. D., Shim, J. J. and Bae, H. K., "Dye Solubility in Supercritical Carbon Dioxide. Effect of Hydrogen Bonding with Cosolvents," *Korean J. Chem. Eng.*, **16**, 111 (1999).

Pederson, C. S., Peterson, W. H. and Fred, E. B., "The Forms of Lactic Acid Produced by Pure and Mixed Cultures of Bacteria," *J. Biol. Chem.*, **68**, 151 (1926).

Schwach, G., Coudane, J., Engel, R. and Vert, M., "Ring Opening Polymerization of D, L-Lactide in the Presence of Zinc Metal and Zinc Lactate," *Polymer International*, **46**, 177 (1998).

Shah, B., Nutan, Schmidt, F. and Nicholas, US patent, **4**, 469674 (1984).

Vlock and Richard, S., US patent, **5**, 165914 (1992).

Xie, R., Wand, D. and Wu, Z., "A Study and Determination on Solubility and Crystalline Water of Calcium Lactate," *J. Chem. Eng. Chinese Univ.*, **5**(2), 152 (1991).

Xue, X. X. and Liu, H. Y., "Experimental Research of Nutrient-Zinc Lactate," *Food Science*, **161**(5), 26 (1993).

Yang, Y. H., He, B., Li, H. L., Qi, Q., Sun, C. and Liu, D., "Study of New Production Technology of Medicine Calcium Lactate," *Henan Science*, **16**(2), 218 (1998).

Zhang, S. P., Zhu, J. and Wang, X. C., "Development of a Novel Nutrient-Zinc Lactate," *Res. Develop. Food*, **3**, 28 (1994).