The Improvement of Melting Characteristics of Capric-Lauric Acid Mixture Employing Prospective Additives for the Cooling Application of Thermal Energy Storage

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A melting point of 18.0 °C for a 65 mol % capric acid - 35 mol % lauric acid (C-L) mixture is considered high for low-temperature thermal energy storage. Chemical additives with low melting points are considered to improve the melting characteristic of the C-L acid. By differential scanning calorimetry (DSC), the effects of chemical additives on the C-L acid in different concentrations have been analyzed. A cryoscopic constant of 10.7 $K \cdot kg_{C-L} \cdot mol^{-1}$ for the C-L acid is obtained. The desired melting depression values of 8 to 11 °C are not met with 0.61 mol each of methyl salicylate, cineole, and eugenol per kg of C-L acid. However, the melting characteristics obtained for the same concentrations of the above-mentioned additives in the C-L acid are applicable for industrial process cooling.

Keywords: *C-L Acid, phase change materials, latent heat storage, chemical additives*

INTRODUCTION

Many studies have been carried out on thermal energy associated with building cooling/heating systems, solar energy collectors, power, and industrial waste heat recovery. Thermal energy storage offers an inexpensive system for the production of energy during off-peak period and provides the cooling capacity during the daytime peak of power consumption. Among the various methods of thermal energy storage, the latent heat storage has valuable advantages. The phase change materials (PCMs) used have high energy density with large cooling effect at a nearly constant temperature.

There are numerous PCMs that have been found and developed. However, several drawbacks have been encountered in the utilization of these PCMs, such as incongruency in melting, nucleation, and supercooling in salt hydrates, and the availability and cost of raw materials for other possible PCMs. Hence, further studies should be done, including the search for new materials.

Fatty acids and other organic substances possess significant characteristics with regards to the required thermodynamics, kinetic and chemical properties. Besides, they have high energy density, with definite melting temperature, and reproducible melting and cooling behavior. Interestingly, 86 g of fatty acids is obtained from 100 g of coconut oil, an abundant source in the Philippines. Fatty acids available in coconut oils have high melting temperatures. Nevertheless, mixtures of miscible materials with different melting points can provide a lower melting temperature. Many researches employing binary mixtures had been previously conducted [Ames, 1990; Cho and Choi, 2000; Feldman et al, 1989; and Himeno et al, 1988]. A recent study [Dimaano and Escoto, 1998; and Dimaano and Watanabe, 2002] has indicated that the mixture of 65 mol % capric acid and 35 mol % lauric acid (C-L acid) is a potential PCM for thermal energy storage. Fifty per cent of the fatty acid is capric acid and 15 % is lauric acid. An equally abundant alternative source of capric acid is goat oil.

For an effective thermal energy storage performance, the material must possess the desired melting temperature. The C-L acid has a melting point of 18°C with a latent heat of 148 kJ/kg. Such melting point is considered high for the cooling application of thermal energy storage. A temperature below 10°C [SEIS, 1981] must be delivered by the storage system in order to maintain a comfortable temperature of 22 to 25°C in a compartment having an ambient temperature range of 30 to 35°C. This requires a melting temperature of about 7 to 10°C for the cold side storage to achieve dehumidification.

The lowering of the melting temperature of a PCM and the improvement of heat transfer characteristics are possible by adding foreign substances that are compatible to the mixture. The researches conducted [Aceves et al, 1998; Dimaano and Watanabe, 2002; Hasnain, 1998; Py et al, 2001; Yoneda and Takashi, 1978; and van der Leeden et al, 1993]] regarding eutectic mixtures and multiple phase change materials

have set off the chances of finding the optimal chemical additive that can lower the melting point of the C-L acid as a base PCM. It is then the objective of this study to determine the compatible organic chemical additives that can lower the melting point of the C-L acid and at the same time maintain a substantial heat of fusion. The melting characteristics of the C-L acid mixture with chemical additives have to be evaluated employing differential scanning calorimetry (DSC) analysis.

MATERIALS AND METHODS

Materials Selection

The thermophysical properties and the solubility of the additive in the C-L acid are of primary concern in the selection of a good chemical additive. The melting point of the C-L acid with chemical additives must be 8 to 11 °C lower than that without additives but with a heat of fusion sufficient enough to sustain an adequate thermal energy for cooling capacity. The other factors to be deliberated upon are the safety and economic features. For the safety considerations, carcinogenic, flammable, toxic, volatile, hazardous vapor emitting and environmentally degrading additives are discarded. Cost and availability are for the economic features.

Aside from those chemicals with unfavorable properties following the aforementioned safety factors, most of the additives with high heats of fusion were eliminated in the selection because of halogen content. It is a known fact that halogenated compounds cause the ozone depletion. However, some of the apparently compatible additives with the C-L acid that have low melting points have low heats of fusion. Others do not even have heats of fusion available in literature. Nevertheless, they were included in the selection for the determination of the still unknown cryoscopic constant of the C-L acid mixture. The cryoscopic constant indicates the extent of the melting point lowering of the C-L acid mixture.

Table 1. Physical properties of chemical additives.

	Melting Point[d] [°C]	Density[d] [kg·m^{-3}]	Specific Heat[a] [kJ·kg^{-1}·K^{-1}]	Heat of Fusion[a] [kJ·kg^{-1}]	Vapor Pressure @ 20°C [Pa]
Benzaldehyde	-26.0	1050.0	1.04	-	105.02[b]
Caproic Acid	-7.8	922.0	2.65	117.8	0.05[c]
Cineole	1.0	927.0	2.30	3.0	90.40[d]
Diethylene Glycol	-11.5	1120.0	2.31	25.1	14.01[c]
Ethyl Benzoate	-34.6	1051.0	1.28	-	25.26[b]
Eugenol	-7.5	1091.0	-	-	23.73[d]
Methyl Salicylate	-8.3	1182.0	1.87	-	0.87[c]
Oleic Acid	-4.5	893.5	2.99	45.3	0.77[c]
Pentadecane	9.9	727.2	3.08	168.0	0.01[c]
Pentanediol	-18.0	1184.0	3.02	3.5	-

[a] - measured
[b] - (Reid, et al., 1987) [13]
[c] - (Perry and Green, 1997) [14]
[d] - (Lide, et al., 1995) [15]

Materials for Analysis

The C-L acid is composed of 65% capric acid and 35% lauric acid, by mole. The readily available additives obtained were caproic acid, cineole, ethyl benzoate, eugenol, oleic acid, pentadecane, pentanediole, benzaldehyde, methyl salicylate and diethylene glycol. Their properties are provided in Table 1. A PCM consisted of the C-L acid, as the base system, and the chemical additives.

Capric acid, lauric acid (both 98% purity), and pentadecane (99% purity) were manufactured by Tokyo Chemicals, Inc. Benzaldehyde, caproic acid (99% purity), eugenol, methyl salicylate, pentanediole, and cineole were produced by Sigma Chemical Co.; ethyl benzoate (99+% purity) was manufactured by Aldrich Chemical Co., Inc.; and the oleic acid, from D & L Industries, Inc.

Methods

The Mettler Toledo DSC821 was used to evaluate the thermophysical properties and melting characteristics of the C-L acid and the PCM mixtures. Nine molality concentrations (0.11, 0.23, 0.35, 0.48, 0.61, 1.37, 2.35, 3.66, and 5.49 mol/kg$_{C-L}$) of each of the chemical additives were individually prepared and made

homogeneous in the C-L acid base system. Each sample weight of 8-15 mg was encapsulated in hermetically sealed aluminum pans. The heating rate was controlled at 2.5 °C/min. A blank curve of the apparatus was always measured with the same conditions as the experimental curves and recorded to compare with and correct the experimental curves generated from the DSC analysis. A minimum of two thermal cyclic runs was conducted for each PCM sample.

RESULTS AND DISCUSSION

Thermal Analysis

The melting characteristics: heat of fusion, melting temperature, melting peak and melting width of the C-L acid system with the corresponding additives in different proportions were analyzed using the DSC821 Mettler Toledo STAR^e 2000 software. The melting temperature corresponds to the onset temperature. The heat of fusion was estimated by numerically integrating the melting curve as programmed in the computer using a linear horizontal baseline.

As the main storage medium, C-L acid was initially analyzed. It was subjected to a series of heating and cooling processes to see

whether the storage capacity remains constant. Identical heating curves were obtained with consistent melting characteristics. DSC results provided a melting point of 18.0 °C, a melting peak of 22.4°C, and a latent heat of 140.8 kJ/kg. The heating curves obtained from the DSC analysis of each sample consisting of the C-L acid mixture with chemical additives presented negligible difference in separate thermal cycling tests. The thermodynamic quantities vary with the composition of the PCM mixture. Representative thermal curves of the PCM mixture are shown in Figure 1.

Temperature Depression

The investigation of the thermodynamic quantities of the mixture involves an in-depth knowledge about the changes that occur in the PCM mixture composed of different additive concentrations. The lowering in the melting point of the C-L acid is related to the effect of the chemical additive solute on the activity of the C-L acid acting as the solvent.

There is high linearity in the melting temperature depression only at low molality concentration of the chemical additive from 0 to 0.61 mole per kg of the C-L acid (mol/kg_{C-L}) (Figure 2).

The slope of the curve is independent of the identity of the chemical additive. The colligative property of a mixture is ideally demonstrated in very dilute solutions. That is why at lower concentration of additives, a more consistent decreasing trend follows a linear correlation between the temperature depression and the concentration of the mixture. From this figure, the cryoscopic constant (K_f) was determined from the simple colligative equation

$$DT_{fus} = K_f ' m \qquad (1)$$

in which

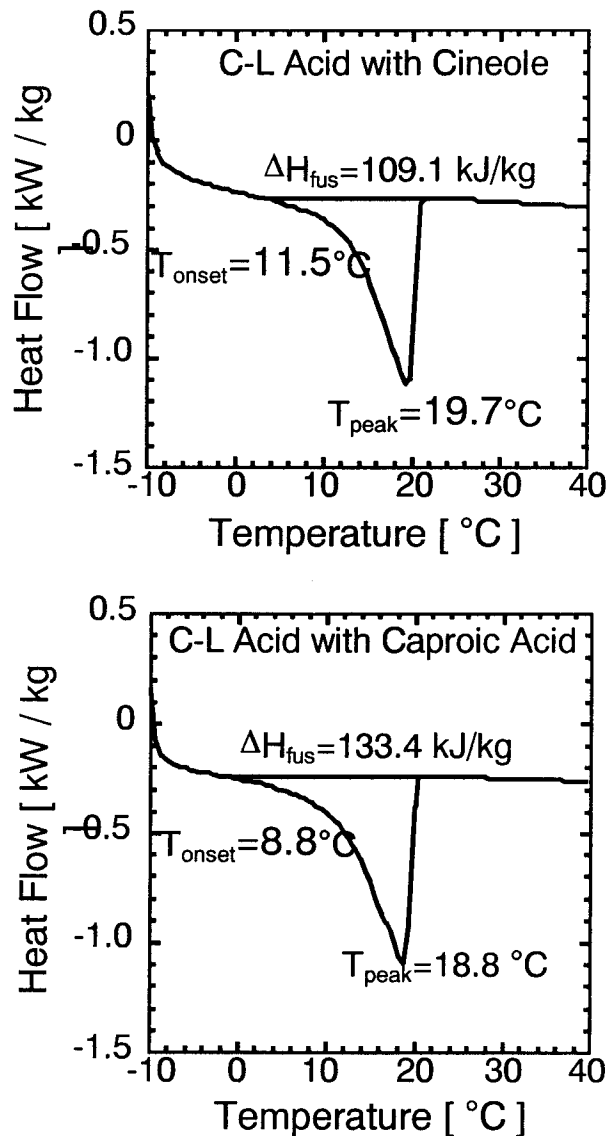$$K_f = \frac{M_1 RT_{fus}^{*2}}{\Delta H_{fus}} \qquad (2)$$

Figure 1. Representative DSC heating curves of 0.61 mol additive in a kg of C-L acid (Xa = 0.10).

The slope obtained from equation (1) provided an average melting point depression constant of 10.7 $K \cdot kg_{C-L}/mol$ that conveys the distinctive characteristic of the C-L acid mixture for all additives. In lower concentrations of additives in the C-L acid, the latter is particularly the solvent while the additives are the solutes. This is valid only at low concentrations since equation (1) was derived from the Gibbs-Helmholtz equation yielding
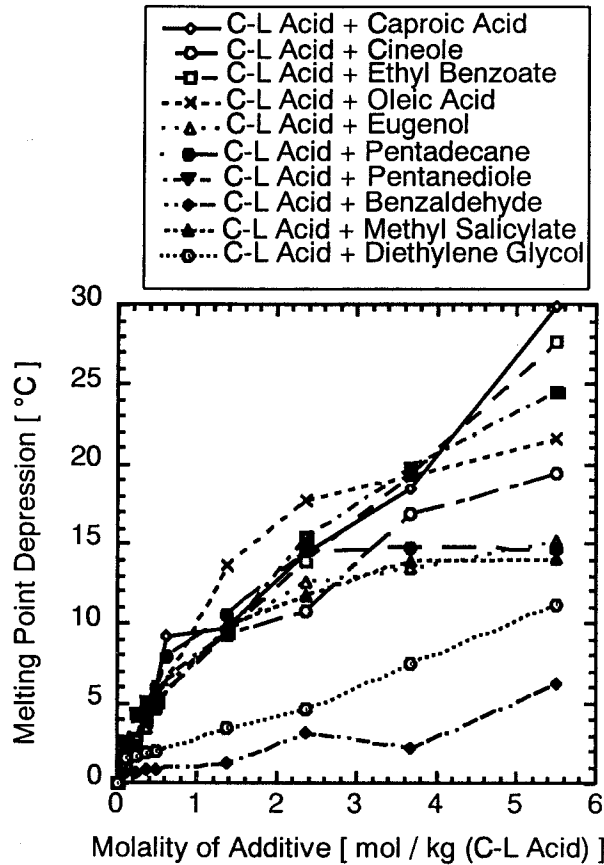
Figure 2. Melting point depression at different molalities of the chemical additive in the C-L acid mixture.

Figure 3. Heat of fusion in the different molalities of chemical additive in the C-L acid mixture

$$\frac{d\ln x_1}{dT} = \frac{\Delta H_{fus}}{RT^2} \qquad (3)$$

$$\ln(1 - x_2) = -x_2 - \frac{1}{2}x_2^2 - \frac{1}{3}x_2^3 - \cdots = x_2 \qquad (5)$$

For very dilute solutions, the heat of fusion ($\mathrm{D}H_{fus}$) of the solvent C-L acid, is assumed independent of temperature over a certain range and equation (3) may be simplified by expressing x_1 (mole fraction of solvent C-L acid) in terms of x_2 (mole fraction of additive) as

$$\ln(1 - x_2) = \frac{\Delta H_{fus}}{R}\left(\frac{T - T_{fus}}{T \times T_{fus}}\right) \qquad (4)$$

The term ln ($1-x_2$) is expanded in a power series and if mole fraction of the additive solute is very small, only the first term is left as
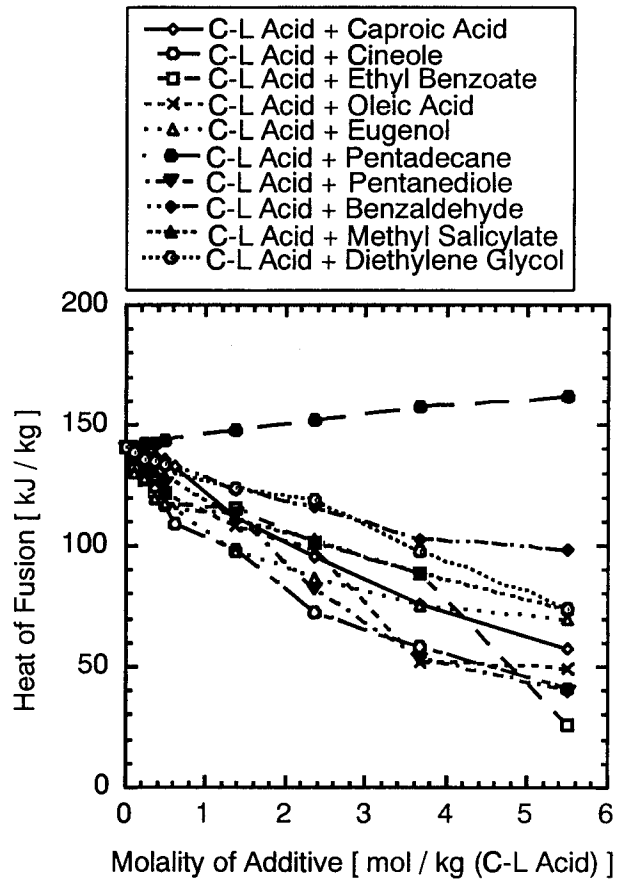
(T-T_{fus}) represents the freezing point depression and considered small such that T $T_{fus} \gg T_{fus}^2$. The slope of the melting depression against the molality sets off to deviate at higher additive concentrations (i.e., beyond 0.61). The deviation from the non-ideal behavior is caused by the enhanced molecular randomness of the solution due to the presence of more additives in the C-L acid system. The temperatures of the mixtures drop variably, with the gradation depending on the additives' tendency to lower the melting point of the C-L acid.

A practically small change in the heat of fusion of the PCM mixture matches with the temperature depression linearity at low additive concentration (i.e., below 0.61 mol/
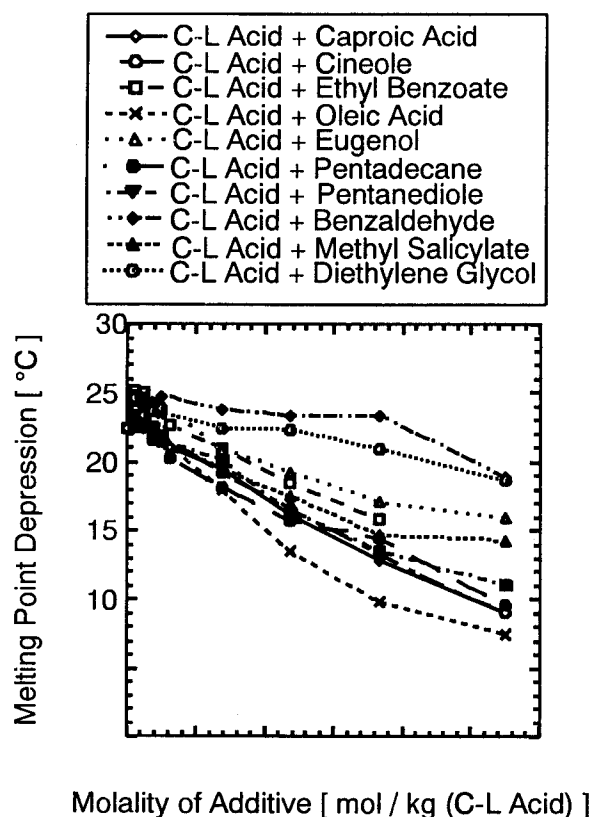
Figure 4. Upper melting band temperature in different molalities of the chemical additive in the C-L acid mixture.

Figure 5. Lower melting band temperature in different molalities of the cnemical additive in the C-L acid

kg_{C-L}) as shown in Figure 3. The degree of the inclination of the heat of fusion with respect to higher additive concentration reveals the complex identity of the mixture. As the concentration of the additive is increased, the system becomes complex. The characteristic of the C-L acid is altered causing the deviation from its ideal condition. The real solvent cannot be distinctly identified due to the existence of more amount of additive in the PCM mixture that at higher additive concentration makes the mixture a defined ternary system.

The increase in ethyl benzoate concentration in the C-L acid furnishes the greatest decrease in DH_{fus} while benzaldehyde and methyl salicylate showed better DH_{fus} at higher concentration as shown in Figure 3. Among the organic chemical additives tested, higher concentrations of pentadecane in the C-L acid
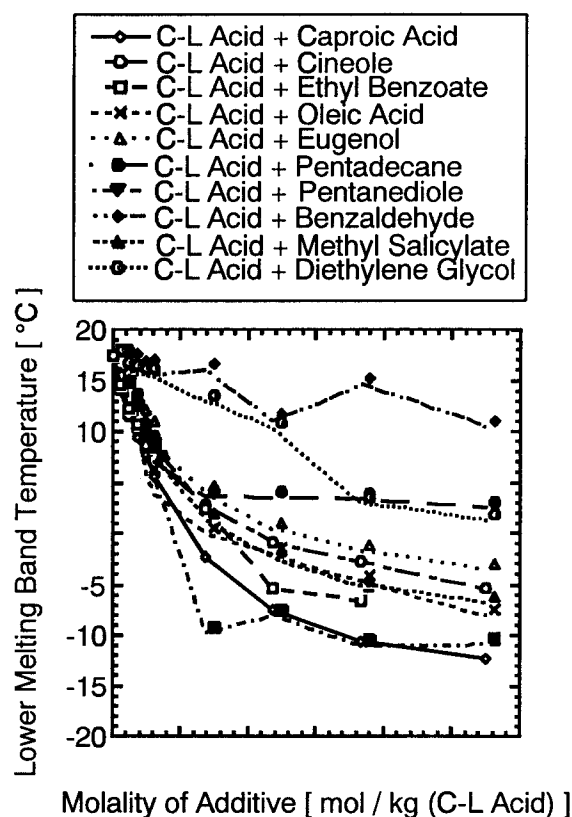
furnished the higher heat of fusion with a lower melting point. However, this combination had been previously investigated and published [12]. It is merely presented here to show its comparative difference with the chemical additives, it being a storage material itself. Oleic acid manifested an irregularity at higher concentrations of 3.7 and 5.5 mol/kg_{C-L}.

For an effective cooling application of a thermal storage system applying C-L acid as the base PCM medium, a melting point depression of 8 to 11°C must be furnished by the C-L acid-chemical additive combination. Benzaldehyde and diethylene glycol exhibited low melting point depression even at higher concentrations compared with the other PCM combinations. All the others manifested the same temperature depression at lower concentrations.
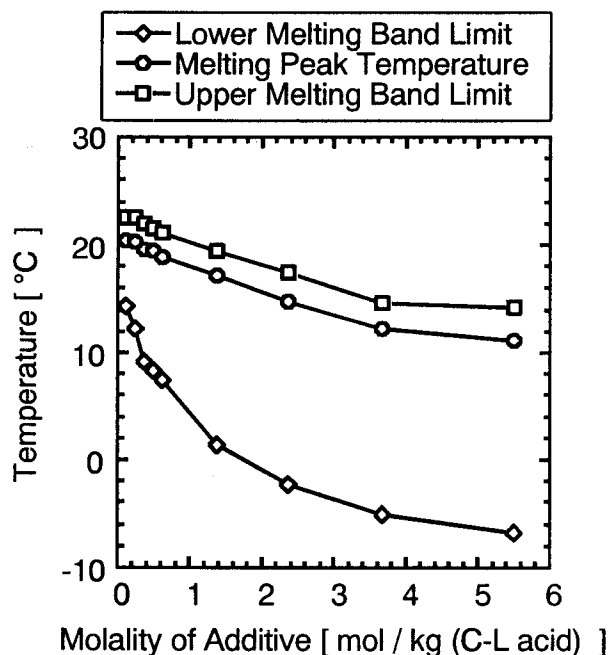
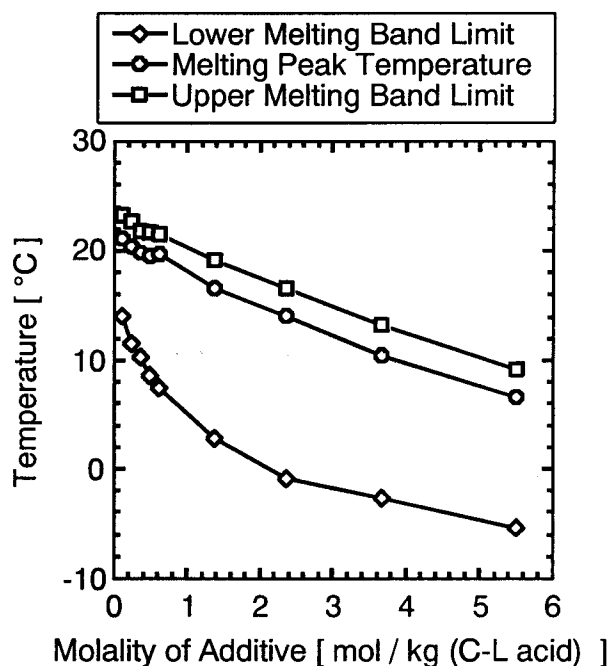**Figure 6.** Melting band width at different molalities of methyl salicylate in the C-L acid mixture.

Figure 7. Melting band width at different molalities of cineole in the C-L acid mixture.

MELTING BAND TEMPERATURE LIMITS

Examining their DSC derived data, all the chemical additives in the C-L acid showed a consistent trend in their upper melting band temperatures at different concentrations (Figure 4). Fluctuations in the lower melting band temperature of C-L acid with benzaldehyde, diethylene glycol, and pentanediol were observed as presented in Figure 5. Ethyl benzoate, on the other hand, demonstrated an obviously lower melting band temperature with a greater melting band width. All PCM mixtures with the additive concentration of 0.61 mol/kg$_{C-L}$, except that with oleic acid, exhibited acceptable lower melting band temperatures.

Consistency in their concentrations is needed in order to confidently decide on the optimum combination of the C-L acid : chemical additive mixture that can provide the best melting characteristics. Reliable information can be obtained from concentrations where high linearity in melting point depression exists. In such case, an additive concentration of 0.61 mol/kg$_{C-L}$ offers

a safe basis for melting characteristics evaluation. Among the chemical additives, the concentration of methyl salicylate, cineole, and eugenol in the C-L acid provided the least melting band width. Supplementary DSC analyses depicting the melting band widths of these PCM mixtures are respectively shown in Figures 6, 7, and 8. On the basis of higher heats of fusion with the manifestation of the agreeable melting temperature depression in the C-L acid mixture, the selection finally boiled down to the C-L acid with methyl salicylate, cineole and eugenol as additives. Except for pentadecane that provided the greatest melting point depression, methyl salicylate offered the highest heat of fusion followed by cineole, and eugenol. A narrow melting band provides a better thermal storage capacity in the PCM. The C-L acid with methyl salicylate presented the narrowest melting band width.

Considering their melting temperatures (Table 2), the desired temperature depression in the C-L acid of 8 to 11 °C was not attained in the additive concentration of 0.61 mol/kg$_{C-L}$ but was observed in the 1.37 mol/kg$_{C-L}$ (refer

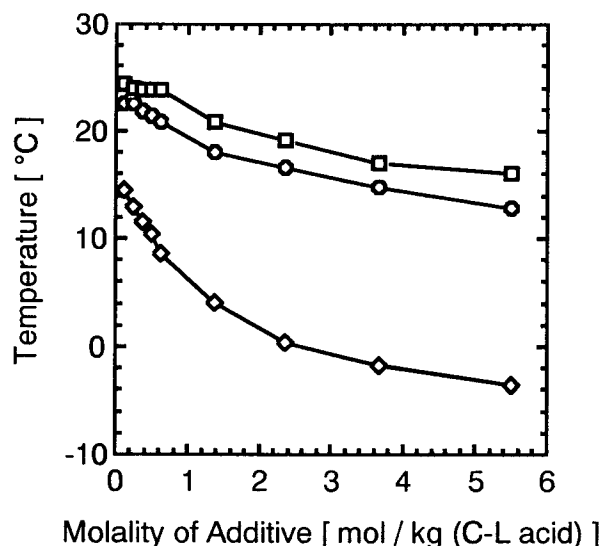Figure 8. Melting band width at different molalities of eugenol in the C-L acid mixture.

Table 2. Melting band temperature limits of C-L acid and its combination with selected chemical additives in 0.6 mol/kg$_{C-L}$ obtained from DSC analysis.

PCM	Melting Band [°C]		Melting Peak [°C]	Melting Temperature [°C]
	Lower Limit	Upper Limit		
C-L Acid + Eugenol	8.6	23.8	20.9	13.0
C-L Acid + Cineole	7.5	21.5	19.7	11.5
C-L Acid + Methyl Salicylate	7.6	18.9	21.3	12.3
C-L Acid	17.5	22.4	24.0	18.0

to Figure 2). Nevertheless, the PCM mixtures with 0.61 mol/kg$_{C-L}$ can be employed for industrial process cooling applications. Other probable organic chemicals that are compatible with the C-L acid must be investigated to come up with the right additive that can meet the required melting point and the heat of fusion for the residential space unit cooling application.

CONCLUSION

The results obtained from the DSC analysis of the different PCM mixtures showed that the C-L acid had a cryoscopic constant of 10.7 K·kg$_{C-L}$/mol, that is the same for all additives. The temperature depression in the C-L acid of 8 to 11 °C was not attained in the available additives that were tested. However, although the PCM mixtures with additive concentration of 0.61 mol/kg$_{C-L}$ were slightly higher for residential use, the acquired data are valuable for future considerations in thermal energy storage. A melting point of about 13 °C is good enough for industrial applications that will focus on waste heat recovery and environmental safety related concerns.

NOMENCLATURE

ΔH_{fus} heat of fusion of C-L acid [kJ·mol-¹]
K_f melting point depression constant [kg·K·mol -¹]
M_l molar mass of C-L acid [kg·mol-¹]
m molality of the PCM mixture [mol·kg -¹]
R universal gas constant [kJ·mol-¹×K-¹]
$T_{fus}{}^*$ melting point of C-L acid [°C]
ΔT_{fus} melting point depression [K] (melting point of C-L acid) – (melting point of the PCM mixture)
x_1 mole fraction of solute additive [-]
x_2 mole fraction of C-L acid [-]

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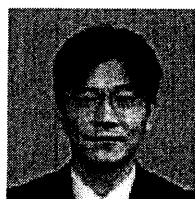
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