Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thermochimica Acta 424 (2004) 1–5
thermochimica acta
www.elsevier.com/locate/tca

Phase diagram of the ternary system lauric acid–capric acid–naphthalene

Jin Longfei*, Xiao Fengping

College of Chemistry, Central China Normal University, Wuhan 430079, PR China

Received 11 September 2003; received in revised form 5 April 2004; accepted 6 April 2004
Available online 28 July 2004

Abstract

The mixture of lauric acid and capric acid is a potential latent heat storage material. However, its eutectic melting temperature is quite high for low-temperature thermal energy storage. Addition of naphthalene is proposed. The ternary system lauric acid–capric acid–naphthalene has been investigated by differential scanning calorimetry (DSC), visual polythermal and chromatography of gases. The phase diagram is of an incongruent eutectic type. The eutectic mixture contains 18.4 mol% lauric acid, 63.1 mol% capric acid and 18.5 mol% naphthalene and melts at 13.3 °C. The peritectic mixture contains 32.4 mol% lauric acid, 48.2 mol% capric acid and 19.4 mol% naphthalene and peritectic temperature of 16.2 °C. The incongruent compound was analysed to be $CH_3(CH_2)_{10}COOH{\cdot}CH_3(CH_2)_8COOH$. The melting temperature of the lauric acid–capric acid–naphthalene eutectic mixture makes it suitable for cooling applications.

Keywords: DSC; Visual polythermal; Chromatography of gases; Lauric acid; Capric acid; Naphthalene; Phase diagram

1. Introduction

Some fatty acids are good phase change materials (PCMs) which have been cited in previous studies [1,2]. At the same time, several innovative methods to utilise these materials such as validated and technically identified as feasible materials to infuse in building materials had been finished [3,4]. All have encouraged others to study its more basic respect [5,6]. In these studies, some hope to improve the melting characteristics of fatty acids by adding other compounds in a solution [7,8]. And the effect of additives on nucleation rate, crystal growth rate and induction time in precipitation presented by van der Leeden et al. [9].

Lauric acid and capric acid have been studied as a potential PCM for cooling applications [10]. And the phase equilibrium of its binary system was studied by Dimaano and Escoto [10], Feldman et al. [1] and Taiping et al. [11]. However, its eutectic melting point is too high to consider it as the cooling purpose of a residential or industrial space unit. In order to get a comfortable temperature of 25 °C in a space unit having an ambient temperature range of 35–38 °C, a temperature below 10 °C must be maintained by the thermal energy storage system to achieve dehumidification. So, the addition of a suitable third substance has been studied. But those chemical additives are not perfect, not only because their price is high but also because their source is limited [5,12,13].

Naphthalene has an inexpensive cost, good chemical stability, regular lowering of the melting point and crystallisability which can prevent fatty acids from undergoing a overcooling phenomenon [14,15]. Thus, the combination of the lauric acid–capric acid and naphthalene is considered in this study to determine the possible lowering of the melting point of the lauric acid–capric acid and to obtain its phase diagram.

We had investigated the phase diagram of naphthalene–lauric acid [15]. It forms an eutectic at 68.3 mol% lauric acid and melts at 35 °C. In this paper, the binary system, naphthalene–capric acid and the ternary system, lauric acid–capric acid–naphthalene, have been studied by differential scanning calorimetry (DSC), visual polythermal and chromatograph of gases.

2. Experimental

Thermal experiments of the melting range of different combinations were performed in the Pekin-Elmer DELTA SERIES DSC 7 instrument. Alumina crucibles and reference

* Corresponding author. Tel.: +86-2767867953; fax: +86-2767867955.
E-mail address: jlf163@public.wh.hb.cn (J. Longfei).

0040-6031/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2004.04.009

material were used. Certified indium wire encapsulated in an alumina crucible (supplied by instrument manufacturer) was used for temperature calibration. The heating and/or cooling rates were 2 °C/min. The temperature range investigated was between 10 and 50 °C and/or 10 and 90 °C.

The melting temperatures of liquidus of the phase diagram were also observed by visual polythermal with a precise thermometer with temperature error ±0.1 °C. The thermometer was previously calibrated against standard substances with known melting points: water + ice (0 °C), carbon disulfide (46.3 °C), diphenylamine (56.1 °C) and phenyl benzoate (70 °C).

A HP-5890(II) gas chromatography was used to analyse the composition of the incongruent compound. The samples of the incongruent compound and standard lauric acid and capric acid (chromatographic grade from Shanghai Chemical Reagent Co.) were prepared in *n*-hexane. The concentrations were about 10%. The compound was separated on a 25 m × 0.2 mm × 0.2 μm HP-101 (methyl siliconefluid) capillary column (from instrument manufacturer). For the determination of the lauric acid and capric acid with standard lauric acid and capric acid as the model compounds, the conditions chosen were: injection volume, 2 μL; injector temperature, 250 °C; flow rate, 2 mL/min helium; oven temperature isothermal for 1 min at 120 °C then programmed at 10 °C/min to 200 °C and maintained for 3 min, then continued at 5 °C/min to 240 °C with a final isothermal period of 2 min at 240 °C.

The materials, lauric acid (99% purity), capric acid (99% purity) and naphthalene (99% purity), were obtained from Shanghai Chemical Reagent Co. For mixtures of systems, certain amounts of components were weighed and mixed in a 50 mL beaker with the aid of one magnetic stirring pebble. Then, the beaker was placed on a magnetic stirring heating machine. The mixtures were heated to melting point, stirring was continued for 15 min and then frozen. The total mass of each mixture was about 10 g and the percentage of each material in the mixtures was calculated based on the actual mass employed.

3. Results and discussion

3.1. The binary system lauric acid–capric acid

For the binary system lauric acid–capric acid, Paris et al. [2] observed that it formed an eutectic at 73 mol% capric acid which melted at 16.6 °C. They also suggested the formation of an incongruent compound at 41 mol% capric acid and its peritectic temperature at 21.5 °C. Neeper [3] stated that lauric acid and capric acid formed an eutectic at 87.7 mol% capric acid which melted at 19 °C. Feldman et al. [1] and Longfei and Deshui [6] considered that the lauric acid–capric acid system in the respective composition ratio of 65 and 35 mol%, exhibited an eutectic melting point of 18.0 °C. As above mentioned, these data have a little difference.

We had also investigated the system by differential scanning calorimetry, visual polythermal and chromatography of gases. The phase diagram is of an incongruent eutectic type. The eutectic mixture contains 79.0 mol% capric acid and melts at 18.3 °C. The peritectic mixture contains 58.9 mol% capric acid and peritectic temperature at 22.4 °C. The incongruent compound is $CH_3(CH_2)_{10}COOH{\cdot}CH_3(CH_2)_8COOH$. The measurements are summarised in the Fig. 1, resulting in the phase diagram of the system, lauric acid–capric acid. In the whole composition range under discussion, two middle thermal effects occur on the DSC curves at temperatures of about 18.3 and 22.4 °C. On the other hand, the effects which originate from melting are strong. At higher temperatures, the system has a multiphase character. Above 18.3 °C, four phases occur: liquid, L; the compounds, lauric acid; $CH_3(CH_2)_{10}$-$COOH{\cdot}CH_3(CH_2)_8COOH$ and capric acid. Via peritectic reaction, the liquid L and lauric acid are used to form crystals of $CH_3(CH_2)_{10}COOH{\cdot}CH_3(CH_2)_8COOH$. Below 18.3 °C, three phases: lauric acid, $CH_3(CH_2)_{10}$-$COOH{\cdot}CH_3(CH_2)_8COOH$ and capric acid occur, meanwhile, the system has a binary character in the composition range 50–100 mol% capric acid. The eutectic temperature obtained (18.3 °C) is higher than that reported in the previous paper [2], and is lower than stated in paper [3] but is about level with the datum of Feldman et al. [1] and Longfei and Deshui [6] as observed. The composition of the eutectic mixture is found to be 79.0 mol% capric acid in about agreement with [1]. These disagreements can be explained. It may due to the fact that the purity of the single acids used in the mixture by the above authors and by us was not the same, and thus, the prepared mixture has different thermophysical properties. The authors also attribute these to the experimental methods. When only DSC measurements were carried out in these works, the heating rate may be considered as one factor which affected the results [16]. Furthermore, the supercooling phenomenon that occurred during thermal experiments of the mixtures can also interfere with the results. So, this study must be observed by visual polythermal and repeated many times.

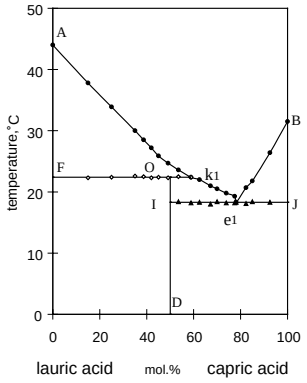

Fig. 1. Phase diagram of the system lauric acid–capric acid.

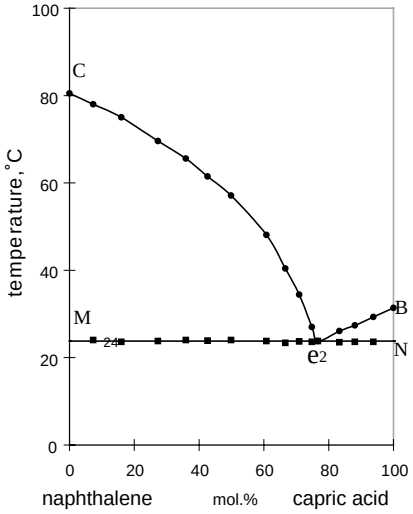

Fig. 2. The phase diagram of naphthalene–capric acid.

3.2. The binary system naphthalene–capric acid

Fig. 2 is the phase diagram of the system naphthalene–capric acid, which is formed from the measurements. It is an eutectic type, being eutectic at 76.7 mol% capric acid and melts at 23.8 °C. In the whole composition range, one middle thermal effect occurs on the DSC curves at temperatures of about 23.8 °C. On the other hand, the effects which originate from melting are strong. At higher temperatures, the system has a multiphase character. Above 23.8 °C, three phases occur: liquid L, the compounds naphthalene and capric acid. Below 23.8 °C, only two phases, naphthalene and capric acid, occur.

3.3. The ternary system lauric acid–capric acid–naphthalene

Thirteen vertical cross sections of the composition triangle, indicated in Fig. 3, were studied. The liquidus curves of these sections are shown in Figs. 4–7. The compositions and the temperatures of deflection points on the liquidus curves are given in Table 1. These data form secondary crystallisation lines. Fig. 8 represents the ternary phase diagram constructed from these projections. In the ternary system, there is one incongruent compound which was analysed to

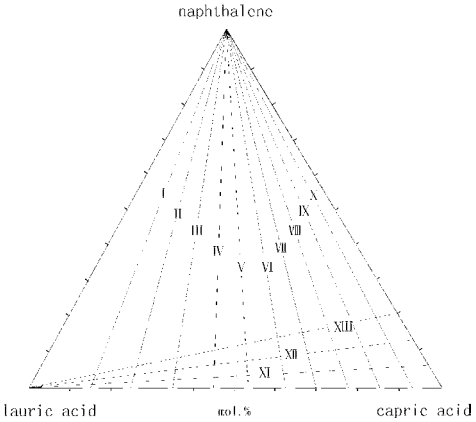

Fig. 3. Positions of 13 vertical sections on the composition triangle.

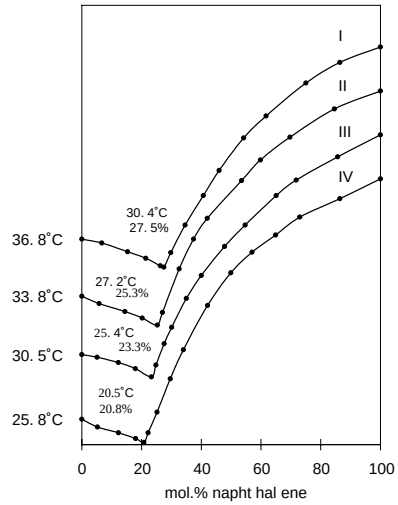

Fig. 4. Liquidus curves for sections I, II, III and IV.

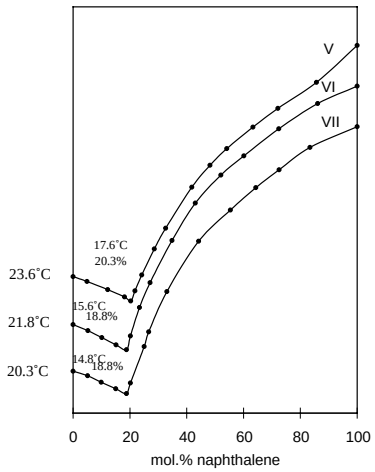

Fig. 5. Liquidus curves for sections V, VI and VII.

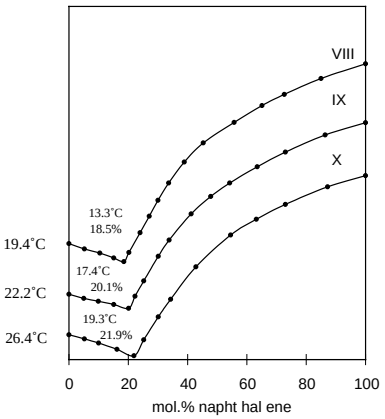

Fig. 6. Liquidus curves for sections VIII, IV and X.

Table 1
Compositions and temperatures of deflection points on the liquidus curves

Section	Composition of the section (mol%)	First point[a]		Second point[a]	
		mol%	T (°C)	mol%	T (°C)
I	(85.0 lauric acid, 15.0 capric acid)–naphthalene	27.5(1)	30.4		
II	(75.0 lauric acid, 25.0 capric acid)–naphthalene	25.3(1)	27.2		
III	(65.0 lauric acid, 35.0 capric acid)–naphthalene	23.3(1)	25.4		
IV	(55.0 lauric acid, 45.0 capric acid)–naphthalene	20.8(1)	20.5		
V	(46.5 lauric acid, 53.5 capric acid)–naphthalene	20.3(1)	17.6		
VI	(37.5 lauric acid, 62.5 capric acid)–naphthalene	18.8(1)	15.6		
VII	(30.0 lauric acid, 70.0 capric acid)–naphthalene	18.8(1)	14.8		
VIII	(22.5 lauric acid, 77.5 capric acid)–naphthalene	18.5(1)	13.3		
IX	(15.0 lauric acid, 85.0 capric acid)–naphthalene	20.1(1)	17.4		
X	(7.5 lauric acid, 92.5 capric acid)–naphthalene	21.9(1)	19.3		
XI	(95.0 capric acid, 5.0 naphthalene)–lauric acid	20.0(2)	17.5	43.6(2)	22.4
XII	(88.0 capric acid, 12.0 naphthalene)–lauric acid	19.6(2)	16.1	41.1(2)	21.2
XIII	(80.0 capric acid, 20.0 naphthalene)–lauric acid	18.6(2)	14.1	37.0(2)	18.9

[a] Naphthalene (1) and lauric acid (2).

be $CH_3(CH_2)_{10}COOH{\cdot}CH_3(CH_2)_8COOH$. So, Fig. 8 is an incongruent eutectic type.

There are four fields of primary crystallisation in Fig. 8. These are bound to each other by the curves of binary eutectic: e_3K(lauric acid + naphthalene), $KE(CH_3(CH_2)_{10}COOH{\cdot}CH_3(CH_2)_8COOH$ + naphthalene), e_2E(capric acid + naphthalene), $e_1E(CH_3(CH_2)_{10}COOH{\cdot}CH_3(CH_2)_8COOH$ + capric acid) with the compounds that crystallise along with them and the one of binary peritectic for which curve k_1K corresponds to the reaction: $CH_3(CH_2)_{10}COOH + L(k_1K) \rightarrow CH_3(CH_2)_{10}COOH{\cdot}CH_3(CH_2)_8COOH$. The eutectic point was determined by extrapolation, which contains 18.4 mol% lauric acid, 63.1 mol% capric acid, 18.5 mol% naphthalene and $E = 13.3\,^{\circ}C$. The peritectic point contains 32.4 mol% lauric acid, 48.2 mol% capric acid, 19.4 mol% naphthalene and $K = 16.2\,^{\circ}C$, which corresponds to the reaction: $CH_3(CH_2)_{10}COOH + L(K) \leftrightarrow C_{10}H_8 + CH_3(CH_2)_{10}COOH{\cdot}CH_3(CH_2)_8COOH$.

It can be concluded from the analysis results of the ternary system that the melting temperature of the lauric acid + capric acid + naphthalene eutectic mixture makes it suitable for cooling applications such as residential building and industrial space unit cooling with respect to the climate conditions.

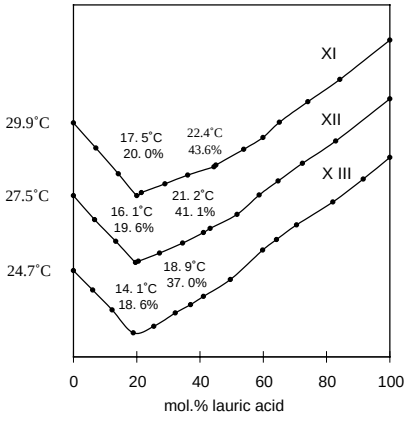

Fig. 7. Liquidus curves for sections VI, XII and XIII.

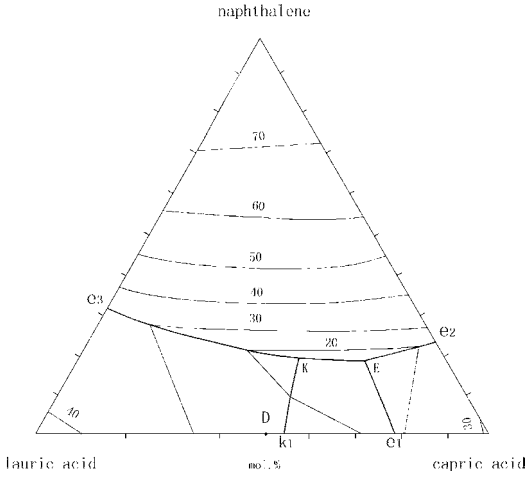

Fig. 8. The phase diagram of lauric acid–capric acid–naphthalene.

Acknowledgements

Authors are grateful to Prof. Ruan Deshui for DSC measured.

References

[1] D. Feldman, N.M. Shapiro, D. Banu, C.J. Fuks, Solar Energy Mater. 18 (1989) 201–216.
[2] J. Paris, M. Falardean, C. Villenueve, Energy Sources 15 (1993) 85–93.
[3] D.A. Neeper, Solar Energy 68 (2000) 393–403.
[4] A.F. Rudd, ASHRAE Trans. 99 (1993) 339–346.

[5] M.N. Roxas Dimaano, T. Watanabe, Energy 27 (2002) 869–888.
[6] J. Longfei, R. Deshui, J. Central Chin. Normal Univ. (Nat. Sci.) 35 (2001) 183–184.
[7] N. Yoneda, S. Takanashi, Solar Energy 21 (1978) 61–63.
[8] S.M. Aceves, H. Nakamura, G.M. Heistad, J. Martinez-Frias, Trans. ASME 120 (1998) 14–19.
[9] M.C. van der Leeden, D. Kashchiev, G.M. van Rosmalen, J. Cryst. Growth 130 (1993) 221–232.
[10] M.N.R. Dimaano, A. Escoto, Energy 23 (1998) 421–427.
[11] Z. Taiping, R. Deshui, Z. Daosheng, H. Qizhu, J. Central Chin. Normal Univ. (Nat. Sci.) 26 (1992) 461–464.
[12] N. Himeno, K. Hijikata, A. Sekikawa, Int. J. Heat Mass Transfer 31 (2) (1988) 359–366.
[13] M.N.R. Dimaano, T. Watanabe, Appl. Therm. Eng. 22 (2002) 365–377.
[14] Chemistry Information Institute, The Handbook of Chemical Products (Organic Compounds), second ed., Chemical Industry Press, Beijing, 1998.
[15] J. Longfei, R. Deshui, J. Central Chin. Normal Univ. (Nat. Sci.) 35 (2001) 183–184.
[16] K.L. Ramakumar, M.K. Sayena, S.B. Deb, J. Therm. Anal. Calorim. 66 (2001) 387–397.