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Solid–liquid phase equilibria of (*n*-octadecane with myristic, and palmitic acid) binary mixtures used as phase change materials (PCMs)

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ABSTRACT

Values of solid–liquid equilibrium (SLE) for the organic binary mixtures of {*n*-octadecane (1) + myristic acid (2)} (eutectic temperature T_E = 299.65 K, eutectic composition x_{1E} = 0.897, latent heat of melting of eutectic mixture $\Delta_{fus}H_E$ = 236 J g^{-1}), {*n*-octadecane (1) + palmitic acid (2)} (T_E = 300.35 K, x_{1E} = 0.950, $\Delta_{fus}H_E$ = 238 J g^{-1}) were measured in this study using differential scanning calorimetry (DSC). Simple eutectic behaviour is observed for these systems. The experimental and predicted solid–liquid phase diagrams investigated in this work are characterised by positive deviations from ideality ($\gamma > 1$). The experimental data are correlated as functions of the temperature using non-ideal solution models, namely, the Buchowski (λh) equation, UNIQUAC, and UNIFAC models, respectively, and satisfactory results are presented.

1. Introduction

Thermal energy storage (TES) is the temporary storage of high or low temperature energy for later use. It bridges the time gap between energy requirements and energy use [1–4]. This effect could be achieved by using phase change material (PCM). PCMs are able theoretically to change state at nearly constant temperature and therefore to store large quantity of energy [5,6].

Organic solid–liquid PCMs have stable phase change temperature (without phase segregation), consequent degradation of latent heat fusion, self-nucleation (no supercooling) and usually non-corrosive [7].

Among organic PCMs, saturated hydrocarbons and fatty acids have been widely studied [8,9]. In general, the longer is the length of hydrocarbon chain, the higher will be the melting temperature. Materials of saturated hydrocarbons are less expensive, non-corrosive and have lower vapour pressure. However, they possess some undesirable properties such as low thermal conductivity, non-compatibility with a plastic container, moderately flammable, and a high volume phase change between the solid and liquid stages. The fatty acids are the compounds of carbon (C), hydrate (H) and oxygen (O). Except for low corrosion activity, other properties of the fatty acid PCMs include high heat of fusion, chemically and thermally stable.

The solid–liquid eutectic PCMs normally consist of two or more components. The main advantage of eutectics over other types of PCMs is that their melting points can be adjusted by combining different components. Lots of fatty acids mixtures [10–17] and few of alkenes mixtures [18,19] have been reported.

However, the number of studies on the latent heat storage by a eutectic PCM is still limited in the literature. As a part of our studies on binary mixtures of aliphatic hydrocarbons and fatty acids [20], in this article, at first, we focussed our attention on the binary mixtures composed of *n*-octadecane with myristic acid, and palmitic acid. The solid–liquid phase diagrams of the binary mixtures were determined by means of differential scanning calorimetry (DSC). Furthermore, the experimental data were correlated as functions of the temperature using non-ideal solution models, namely, the Buchowski (λh) equation, UNIQUAC, and UNIFAC models, respectively, and to investigate the performance of these expressions for correlation or predicting solid–liquid equilibrium (SLE) of those two binary systems.

2. Experimental

2.1. Materials

All chemicals of *n*-octadecane, myristic acid, and palmitic acid were obtained from J&K Scientific Ltd. (Beijing, China). The purity of substances, checked by DSC (Mettler DSC30), was not less than

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0.99 mol fraction. The specifications of these chemicals are listed in Table 1. DSC purity determination was based on the van't Hoff's law of melting point depression and carried out under an atmosphere of nitrogen. A detailed description of the purity determinations by DSC is given in ref [21]. Their melting temperatures and enthalpies of fusion were measured using DSC. The melting points of the pure compounds are in close agreement with literature values and no further purification was carried out. Properties of pure compounds, T_m, the melting temperature; and $\Delta_{fus}H_m$, the molar enthalpy of fusion at T_m are listed in Table 2 together with those reported in the literature [22–31].

2.2. Equipment

The measurements were carried out on a Mettler DSC30 differential scanning calorimeter at a constant heating rate of 1 K min^{-1} under purge nitrogen gas at a flow rate of 50 cm^3 min^{-1}. This scanning rate was low enough to approach the equilibrium measurement conditions. Before analysing, the heat flow calibration was done using high purity indium (99.999%, heat of fusion, 28.45 J g^{-1}), temperature calibration was done using *n*-decane, naphthalene and indium (melting points at 243.35 K, 353.25 K and 429.75 K, respectively). The uncertainties of the measurements were estimated to be ±0.2 K for the temperature and ±2% for the enthalpy.

2.3. SLE sample preparation and measurement

For each binary system, the sample preparation and SLE measurement were described in detail previously [32,33]. Small amounts of solid about 5 mg (weighing precision ±0.2 mg, using a Sartorius A200S balance) were taken and sealed in a Mettler sample crucible for the analysis and an empty pan was used as a reference. The uncertainties in terms of mole fraction did not exceed ±0.0005. Before each measurement, samples were subjected to three consecutive cooling and heating cycles between 270 K and 350 K at a scanning rate of 1 K min^{-1}. This pre-treatment was performed in order to avoid thermal memory and polymorphic effects.

3. Results and discussion

3.1. Determination of solid–liquid phase diagrams

Figs. 1 and 2 contain the phase diagrams of the systems (*n*-octadecane + myristic acid), and (*n*-octadecane + palmitic acid) respectively, and found to be of the simple eutectic type. Tables 3 and 4 show the temperatures of the phase transition and melting of the systems studied here along with the enthalpies associated with the eutectic reaction for varying mole fractions of *n*-octadecane, x_1.

For the two binary systems, Tammann's plots are shown in Figs. 3 and 4. From the characteristic Tammann's plots [34], the eutectic compositions are estimated by the intersection of the two *liquidus* curves by extrapolation and then localised with more precision by the determination of the enthalpy of each eutectic reaction. Thus, the eutectic composition and enthalpy of fusion at the eutectic point of the {*n*-octadecane (1) + myristic acid (2)} system were accurately determined: $x_{1E} = 0.897$, and $\Delta_{fus}H_E = 236$ J g^{-1}, respectively. The eutectic temperature determined from all appropriate DSC curves is $T_E = 299.65$ K. Those for (*n*-octadecane + palmitic acid) are $x_{1E} = 0.950$, $\Delta_{fus}H_E = 238$ J g^{-1}, and $T_E = 300.35$ K, respectively.

Experimental solid–liquid equilibria investigated in this work are characterised mainly by the following: positive deviations from ideality are found, thus the activity coefficient, γ, is greater than 1 (see the values of activity coefficients in Tables 2 and 3; ideal solution, $\gamma = 1$).

3.2. Correlation by the Buchowski (λh) equation and UNIQUAC model

3.3.1. Buchowski (λh) equation

The λh equation, which was originally proposed by Buchowski et al. [35], practically could be applicable to most solid–liquid

Table 1
Specification of chemicals in this work.

Chemical name	Source	Initial mass fraction purity[a]	Purification method	Final mole fraction purity[b]	Analysis method[c]
n-Octadecane	J&K	>0.99	None	0.995	DSC
Myristic acid	J&K	>0.99	None	0.990	DSC
Palmitic acid	J&K	>0.995	None	0.992	DSC

[a] Supplier purity.
[b] Standard uncertainty of mole fraction purity is 0.002.
[c] Purity determined at $p = 0.1$ MPa. Standard uncertainty of pressure is 10 kPa.

Table 2
Physical constants of pure compounds: $\Delta_{fus}H_m$, and T_m, denote the molar enthalpy of fusion, the melting temperature, respectively.

Compound	IUPAC name	CAS RN	Formula	Mol. wt.	$\Delta_{fus}H_m$/(kJ mol^{-1})		T_m/K	
					This work	Literature	This work	Literature
n-Octadecane	*n*-Octadecane	593-45-3	$CH_3(CH_2)_{16}CH_3$	254.49	61.65	60.1 [22] 60.760 [23] 61.500 [24] 61.7 [25] 61.706 [26]	300.95	301.0 [23] 301.1 [22] 301.15 [26] 301.35 [25] 301.5 [24]
Myristic acid	*n*-Tetradecanoic acid	544-63-8	$CH_3(CH_2)_{12}COOH$	228.37	44.75	40.1 [27] 45.10 [28] 45.75 [29]	327.15	326.2 [29] 326.6 [27] 327.37 [28]
Palmitic acid	*n*-Hexadecanoic acid	57-10-3	$CH_3(CH_2)_{14}COOH$	256.42	52.55	51.37 [30] 53.9 [31]	335.15	332.7 [30] 335.4 [31]

Standard uncertainties u are $u(T) = 0.2$ K, $u(H) = (0.02 \cdot H)$ J mol^{-1}.