

# Enthalpy of melting and solidification of sulfonated paraffins as phase change materials for thermal energy storage

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## Abstract

Paraffins are used as phase change material (PCM) for latent heat thermal energy storage (LHTES). The efficiency of a PCM is dependent on the encapsulated quantity and energy storage capacity per unit mass during its melting and solidifying. Two different kinds of paraffin (docosane and hexacosane with melting points of 317.15 and 329.45 K, respectively) were sulfonated at three different mole percentages to increase the LHTES efficiency for this purpose. The sulfonation of paraffin samples was proven by Fourier transform infrared (FT-IR) spectroscopy. Adiabatic Bomb Calorimetry was used to determine sulfonation percentages of paraffin samples. Enthalpies of melting and solidifying of docosane, hexacosane, and their sulfonated derivatives were measured by differential scanning calorimetry (DSC) method. Thermal properties obtained by the DSC analysis indicated that the enthalpy of melting and solidifying of docosane and hexacosane could be extended by sulfonation.

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## 1. Introduction

Latent heat thermal energy storage is one of the most favorable ways of thermal energy storage considered for renewable energy source utilization as in solar photothermal systems. Heat is stored mostly by means of the latent heat of phase change of the medium. The temperature of the medium remains more or less constant during the phase transition. A large number of materials have been identified for low intermediate, and high operating temperatures for application as LHTES media. For application of a material as a phase change thermal energy storage medium, information about its latent heat of phase transition as well as densities and specific heats is necessary [1]. High latent heat is required to provide a higher thermal storage per unit weight. High density is desirable to allow a smaller size of storage container, and higher specific heat is preferred to provide for better sensible heat storage.

Solid–liquid PCMs are often used for heat storage applications. Examples include water, salt hydrates, paraffins, certain hydrocarbons and metal alloys. Salt hydrate phase change mate-

rials used for thermal storage in space heating and cooling applications have low material costs, but high packaging costs. A more economic installed storage may be possible with medium priced, high latent heat organic materials suitable for low cost packaging, i.e. those that are insoluble in water and un-reactive with air and some of the common packaging films [2].

Among the solid–liquid PCMs, paraffins offer some significant advantages over other PCMs. They have mass based latent heats and varied phase change temperatures giving flexibility to choose proper PCMs for different LHTES applications. They do not show phase separation after repeated cycling across the solid–liquid transition. Vapor pressures of paraffins are very low. When paraffins are microencapsulated, the convection heat transfer caused by melted paraffin is negligible. They are produced in substantial quantities by the chemical process industry and thus they are readily available and inexpensive.

On the other hand, in recent times, form-stable composite PCMs with basis of polymer has been developed as novel PCMs due to the advantages of preventing the leakage of melted PCM when the composite subjected to solid–liquid phase change process [3–7]. Moreover, paraffins as PCMs were encapsulated to obtain form-stable composite PCMs by using some polymer materials such as styrene butadiene styrene and high density polyethylene [6,8–10].

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For the last 40 years, polymer scientists have been examining an interesting group of the polymer family; ionomers. Most ionomers consist of two phases; one a matrix phase containing dispersed ionic multiplets, i.e. nano size aggregates of interacting ion pairs and the other; an ion rich, more chain entangled cluster 'phase' that consists of regions of restricted chain mobility surrounding the multiplets [11,12]. The ionic group attached to the polymer backbone is generally a functional group of sulfonate, carboxylate or phosphonate in ionomers these types of structures are called as anionic ionomers. Sulfonation reaction is a substitution reaction in order to insert  $-\text{SO}_3$  group via chemical bond to carbon [13,14].

This work focuses on increasing the enthalpy of melting and solidifying of paraffin to increase its LHTES capacity by sulfonation at ionomer level.

## 2. Experimental

### 2.1. Materials

Paraffins (Aldrich), sulfuric acid (98%–Riedel de Hein), 1,2-dichloro ethane (Rathburn Chemicals), acetic anhydride (reagent grade), toluene (Merck), methanol (Merck) were used without further purification.

### 2.2. Sulfonation of paraffins

The sulfonation method is a standard procedure performed by forming acetyl sulfonate from sulfuric acid and acetic anhydride in 1,2-dichloroethane solution of paraffin [15]. The degree of sulfonation was determined by titration and adiabatic bomb calorimetry.

### 2.3. Determination of degree of sulfonation by heat of combustion (calorific) value

Calorimetry is the measurement of the heat flow or energy arising from chemical or physical changes in a material. In spite, the common methods for the determination of sulfonation degree are such as NaOH titration method or AAS sulfur determination [13,16,17], calorimetry is found as an advantageous method for its good reproducibility and the rapidness of the analysis. Bomb calorimeter obeys the regulations of the standard test method of ASTM D 2015-93 (dry basis). A reaction is followed by the measurement of a temperature change as a function of time [18]. The standard method of adiabatic bomb calorimetry including igniting and burning the sample is performed under pressurized excess oxygen atmosphere in order to reach complete combustion. This is a reliable method for the determination of heat content of many fuels and some materials [19–21].

A LECO – adiabatic calorimeter system – C4000 was used for the determination of calorific values. The thermal and thermochemical corrections applied is in accordance with the ASTM D 2015. A 30 bar pure oxygen was applied for complete combustion. The heat of combustion produced increased the temperature of the calorimeter system. The temperature rise is then mea-

sured and used to calculate the gross calorific value [22,23]. The measurements were corrected according to the equation below:

$$Q_v = \frac{(tC) - e_1 - e_2 - e_3}{g} \quad (1)$$

where  $Q_v$ ,  $t$ ,  $C$ ,  $e_1$ ,  $e_2$ ,  $e_3$ , and  $g$  are gross calorific value (cal/g), corrected temperature rise, heat capacity (cal/°C) (°C), correction for the formation of nitric acid (1 mL  $\text{Na}_2\text{CO}_3 = 5.56$  cal), correction for heat of combustion of ignition wire (1 cm = 0.7 cal), correction for heat of formation of sulfuric acid [(23.75%  $\times m_{\text{sample}}$ )/1.8 cal], and mass of sample (g), respectively.

### 2.4. DSC analysis

Thermal properties of paraffin such as melting and solidification points, and latent heats were measured by DSC technique (SETARAM DSC 131). Indium was used as a reference for temperature calibration. The analyses were performed between the temperatures of 20 and 100 °C at 5 °C/min heating rate under a constant stream of argon at flow rate of 60 mL/min. The temperature accuracy was  $\pm 0.1$  °C, and heat flow repeatability was 0.2  $\mu\text{W}$ . A 5–10 mg of sample was sealed in an aluminum pan. The melting and solidification point were taken as onset temperature obtained by drawing a line at the point of maximum slope of the leading edge of the DSC peak and extrapolating base line on the same side as the leading edge of the peak. The latent heat of PCM is determined by numerical integration of the area of the peak of thermal transition. All DSC measurements were repeated three times for each sample. The standard deviation was found to be  $\pm 0.14$  °C in phase change temperature and  $\pm 1.82$  J/g in latent heat values.

## 3. Results and discussion

Fig. 1 shows FT-IR spectra of docosane and 3.59%, 2.95%, and 2.01% sulfonated docosanes in KBr as Fig. 2 shows FT-IR spectra of hexacosane and 1.14%, 0.47%, 0.04% sulfonated hexacosanes in KBr.

It is clear from Figs. 1 and 2 that, sulfonation of paraffin samples results in OH absorption peaks at around  $3450\text{ cm}^{-1}$  in both docosane and hexacosane due to the sulfonic acid groups. The intensity of the peak increases as the level of sulfonation increases. Also sulfonation reaction brings about conjugation in olefinic chains giving stretching vibrations at around  $1600\text{ cm}^{-1}$  in both of the spectra.  $\text{SO}_2$  stretching peaks of sulfonated derivatives of docosane and hexacosane can be seen at around  $1167\text{ cm}^{-1}$  in both figures showing FT-IR spectra of sulfonated derivatives of docosane and hexacosane.

Applicability of adiabatic bomb calorimeter for the determination of degree of sulfonation is checked by comparing the titration results with that of theoretical combustion enthalpies from bond energies. Theoretical heats of combustion reactions can be calculated from Eq. (2) by using bond energies taken from literature [24,25]. Scheme 1 gives combustion reactions of docosane, one unit sulfonated docosane, hexacosane, and one

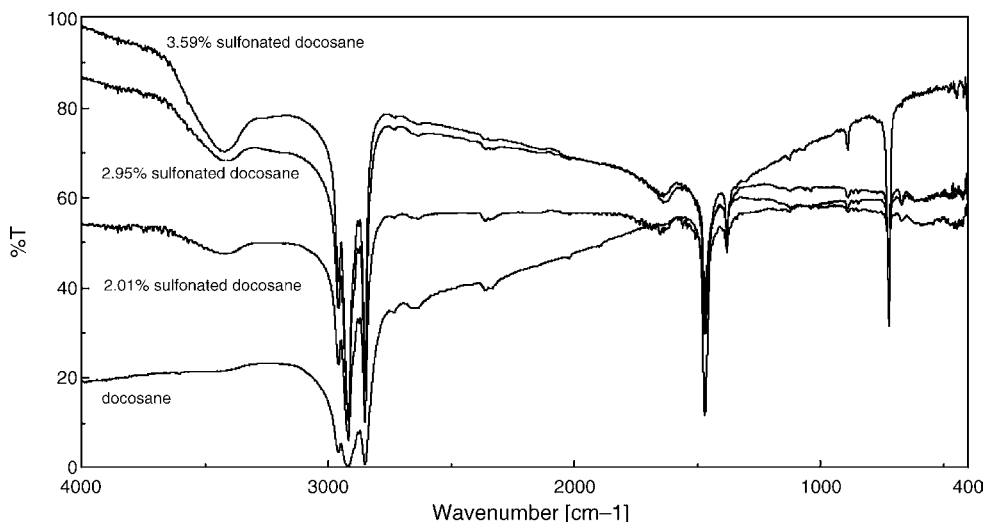


Fig. 1. FT-IR spectroscopy of docosane and its 3.59%, 2.95%, and 2.01% sulfonated derivatives in KBr.

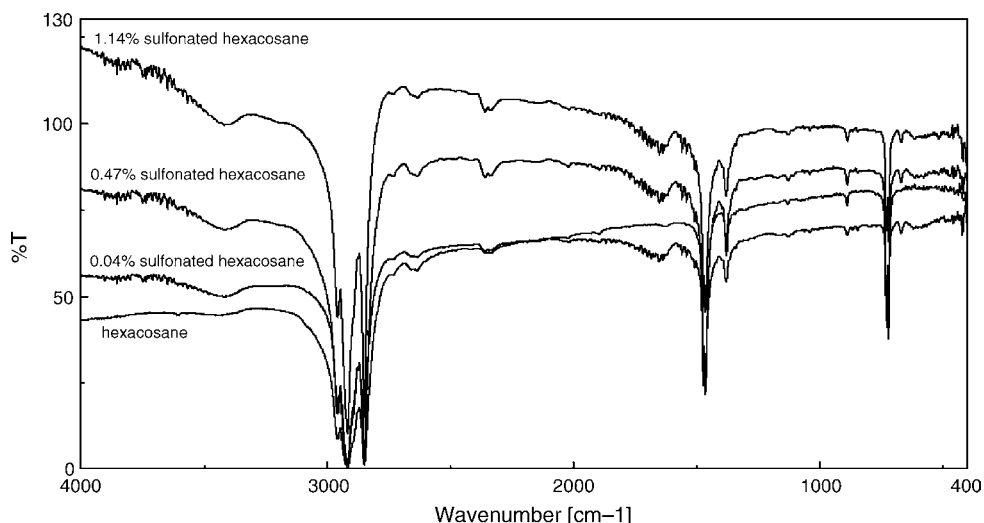


Fig. 2. FT-IR spectroscopy of hexacosane and its 1.14%, 0.47%, 0.04% sulfonated derivatives in KBr.

unit sulfonated hexacosane.

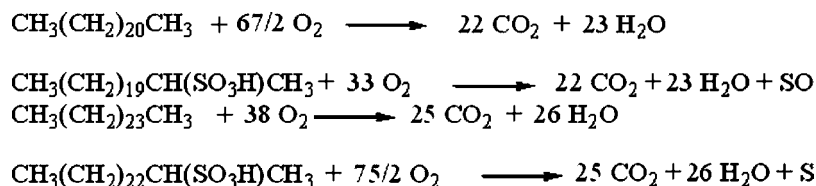
$$\Delta H_{\text{combustion}} = \Delta H_{\text{bonds-formed}} - \Delta H_{\text{bonds-broken}} \quad (2)$$

The graphs obtained by plotting theoretical combustion enthalpy values versus sulfonation degree (%) produced almost linear relationships with  $R^2$  values of 0.9718 and 0.9767 for docosane and hexacosane, respectively. Sulfonation degrees were determined by using calorific values of samples measured by the adiabatic calorimeter in the best line equations of these relationships (Fig. 3).

Table 1 summarizes the combustion heat values of sulfonated samples and calculated sulfonation degrees from the theoretical graphs given in Fig. 1.

The main reason for choosing adiabatic bomb calorimeter for the determination of the degree of sulfonation is that, the adiabatic bomb calorimetry is a simple and more accurate method with no solvent and indicator requirement.

Figs. 4–7 represent DSC curves for docosane, 3.59% sulfonated docosane, hexacosane, and 1.14% sulfonated hexacosane, respectively. Sulfonated samples with maximum enthalpy increment are given as example. In DSC thermograms,



Scheme 1. Combustion reactions of paraffin and sulfonated paraffins.

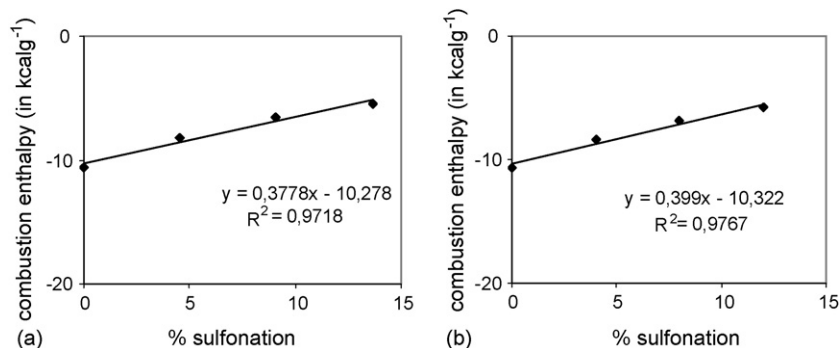


Fig. 3. Theoretical sulfonation degree vs. calorific value relationships for (a) docosane and (b) hexacosane.

Table 1

Heat of combustion values for docosane, hexacosane and their sulfonated derivatives

Heat of combustion measured by adiabatic calorimetry (cal/g)	Degrees of sulfonation
-8,922	3.59% sulfonated docosane
-9,164	2.95% sulfonated docosane
-9,519	2.01% sulfonated docosane
-10,620	Docosane
-9,867	1.14% sulfonated hexacosane
-10,135	0.47% sulfonated hexacosane
-10,307	0.04% sulfonated hexacosane
-10,610	Hexacosane

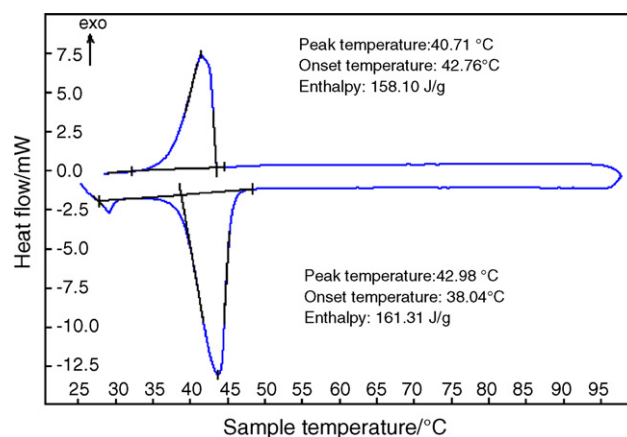


Fig. 5. DSC curve of 3.59% sulfonated docosane.

the sharp peaks represent solid–liquid (melting) or liquid–solid (solidification) phase change as the minor peak correspond to solid–solid phase transition.

When compared to the phase change temperatures, melting points in the docosanes and hexacosanes changed by 0.05 and 0.22 °C, respectively, as freezing points changed by 0.50 and 0.22 °C, respectively. The change in melting and freezing points of sulfonated paraffins tended to increase in general and it is due to sulfonic acid interactions. In addition, such small increases are not significant for LHTES in practice. Similarly, the latent heat of fusion values increased by sulfonation as 8.12 and 24.32 J/g for docosane and hexacosane, respectively, and latent heat of

solidification increased by sulfonation as 5.44 and 15.51 J/g for docosane and hexacosane, respectively.

The difference between paraffins and their sulfonated samples is mainly caused by the chemical nature of intermolecular interactions. The changes in the latent heats are accounted for the physical interaction as hydrogen bonding in sulfonated paraffins. Structural features of ionic paraffin and completely covalent paraffins are quite different from each other. The concentration of bound ions is an important parameter for enthalpies and the most interesting features of ionic paraffins is the state of aggregation of the ionic bonds. Thus, melting and solidification of

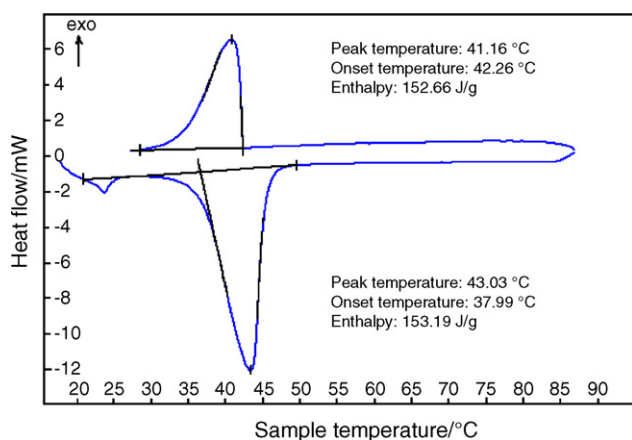


Fig. 4. DSC curve of docosane.

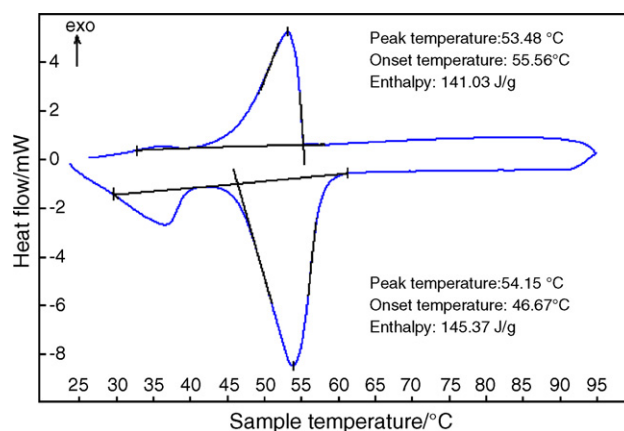


Fig. 6. DSC curve of hexacosane.

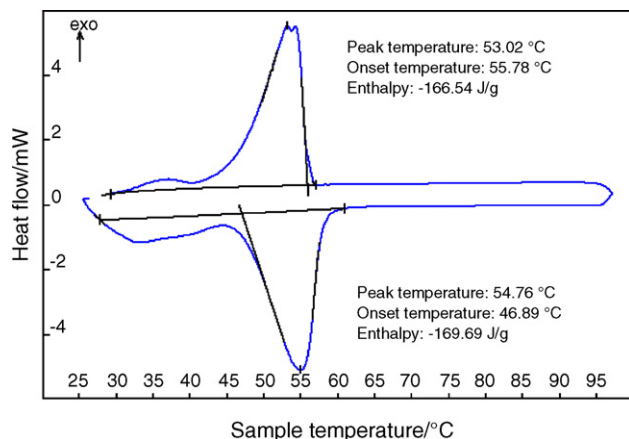


Fig. 7. DSC curve of 1.14% sulfonated hexacosane.

ion pairs, ion multiples, ion-clusters and aggregates certainly will require more energy and this is why latent heat enthalpy values are higher than paraffins.

On the other hand, as paraffin samples for form-stable PCMs are generally encapsulated by non-ionic polymeric materials like polyethylene and polypropylene which have low heat transfer coefficients, sulfonated paraffin samples may be encapsulated by more ionic polymers having higher heat transfer coefficients at higher mass ratios due to the ionic interactions.

#### 4. Conclusion

Docosane and hexacosane were sulfonated in three different mole percentages and characterized by FT-IR spectroscopy successfully and the percentages of sulfonations were determined by adiabatic bomb calorimetry. Thermal analysis by DSC revealed that the sulfonated paraffin samples absorbed and dissipated more energy than the pure paraffin samples used in this study during melting and solidifying. In addition, the changes in the melting and freezing points of sulfonated docosane and hexacosane were not significant. Therefore, sulfonation was found as a suitable method to increase LHTES capacity of paraffins.

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