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The prediction of heat storage properties by the study of structural effect on organic phase change materials

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Abstract

In this study, organic compounds with different structure were investigated, their latent heats of fusion, melting points and thermal stabilities were measured, and as the final step, trends in structure effect on compound properties were derived. The spectrum of measured compounds is wide including hydrocarbons and their derivatives such as alkanes, alcohols, amines, carboxylic acids, dicarboxylic acids, aromatic hydrocarbons etc. All measured results were transparently processed and arranged in charts and figures, so derived trends can be easily read. Both, the chain length and the functional group position on the hydrocarbon chain influence the melting point and latent heat value. Different phenomena, such as polymorphism of the alkanes or packing effect on the carboxylic acids, were observed. The melting point appears to increase with the chain length for most of the measured compounds. Such dependence has not been demonstrated in the effect of chain length on the latent heat value. Moreover, this paper is a source of thermodynamic data such as the latent heat of fusion, melting point, supercooling and thermic stability of different organic phase change materials within the melting temperature range between -5 – 80°C.

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Keywords: Phase-change materials; energy storage; latent heat of fusion; melting point; structure effect

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1. Introduction

Recently, phase-change materials (PCM) became an important phenomenon, because of their great ability to conserve energy and lower the energy consumption through its efficient use and reducing the mismatch between supply and demand. [1] The vast amount of considerable organic compounds and the impossibility of finding

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experimental values of properties for the compounds of interest in the literature raise the need to predict the thermo-accumulation properties avoiding the time consuming analysis.

The biggest advantage of organic compounds compared to inorganic compounds is that they melt without phase segregation, crystallize with lower or no supercooling, are non-corrosive and possess high thermal storage density. On the other hand, many of the organic compounds are flammable and volatile and the heat conduction of hydrocarbons is very low. [2, 3, 4]

The most important properties, which supposed to be evaluated, are the melting point, latent heat of fusion and thermal stability. Suitable melting points are important for the purpose of usage. Thus PCM with a melting point of 60°C is not desired for air conditioning, but rather for an overheating protection or thermal energy storage. The higher the latent heat value, the bigger amount of thermal energy per kilogram of compound can be accumulated. Therefore the high latent heat value also reduces the size and weight of the latent heat storage unit. Thermal stability ensures the long-term life performance of the latent heat storage system, which is important also for the economics of operation.

1.1. Theory of prediction of the thermodynamic properties

In the past, different approaches to estimate thermodynamic properties based on the substance structure have been derived. So called QSPR methods (quantitative structure property relationship) have been used for many different purposes for instance for entropy or density estimations. [5]

Generally there are two basic approaches of the property-structure derivation. Methods based on quantum descriptors and parameters and methods based on group contributions. The former requires a good selection of descriptors and choice of specific predictive model, which both influence the accuracy of the prediction [10], the latter require database of known values, which may not be available for complex molecules and there is no definite standard for fragmenting a molecule. [7]

One of the group contribution methods for thermodynamic property estimation of pure organic compounds was presented by Marrero et al. [6] The contribution value is defined for each molecular fragment and the final value consists of the total sum of all molecular fragment contributions. The approximation is made on three levels depending on the structure size, complexity and simplicity of the molecule.

Another group additive method was developed by Chickos J. S. and Acree Jr. W. E. [8]. The enthalpy of fusion of organic compounds here is conducted from the melting point and the entropy of fusion counted from group parameters. This work summarizes around 1000 measured latent heat values and compares this data with estimated results.

Bo Lian and S. H. Yalkowsky [7] invented a simplified approach to obtain the heat of melting based on prediction of the entropy of melting from three structure-describing parameters: Rotational symmetry, Molecular flexibility and Molecular eccentricity. In their opinion this method provides relatively objective and accurate latent heat values with root mean square error 4,08 kJ/mol and absolute average error 3,03 kJ/mol and R square 0,57. The melting point has to be measured, or taken from a reference; therefore a database of melting points is needed.

L. Bai et al. presented the heat of fusion prediction of ionic liquids based on quantum chemistry structure parameters. From the first six-descriptor model for heat of fusion, the final linear correlation equation with two parameters was derived with the standard deviation of 3.343 and a correlation coefficient of 0,973. It was established, that the latent heat of ionic liquids is greatly dependent on the dipole moment between the cation and anion and on the increasing molecular volume. The large van der Waals forces in the molecule increases the latent heat of fusion. [9]

Goodarzi’s work compares different approaches of correlation. [10] Five, structure-based parameters were selected and methods like multiple linear regression (MLR), artificial neural network (AAN) and Bayesian regulation artificial neural network (BRANN) were predicted. The BRANN method had the best match with experimental values.

2. Measurment of analysis

The most used techniques applied by researchers to establish thermal properties of PCM are differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

2.1. Differential scanning calorimetry (DSC)

In this study, the simultaneous DSC-TGA method was applied (SDT Q600, TA instruments) for the investigation of the melting point and latent heat of fusion. All analysis was processed in the open platinum pan in dry air flow of 100 ml/min with cooling/heating rate of 10°C/min. The data were collected in the temperature range between 30°C below and the temperature 30°C above the expected melting point of the measured sample.

2.2. Thermogravimetric analysis (TGA)

With the data obtained from TGA method was the thermal stability of the sample examined. Sample quantities of 4 – 7 mg were used for measurement. The weight loss, latent heat value decrease and melting point change during five cycles of heating/cooling were observed. By the analysis of the data, the thermal stability was derived. For stable PCMs the observed parameters did not change during measurement. The measuring conditions were the same as during DSC (air flow of 100 ml/min, cooling/heating rate of 10°C/min). The chemical stability after five cycles can be evaluated by FT-IR spectroscopy, but such an evaluation has not been carried out in this study.

3. Results

3.1. Melting point

Initially the melting points of straight chain alkanes with the carbon atom number from 13 to 24, alcohols with 13 to 22 carbon atoms, carboxylic acids with carbons from 12 to 22, three amines, four ethers and six esters were measured.

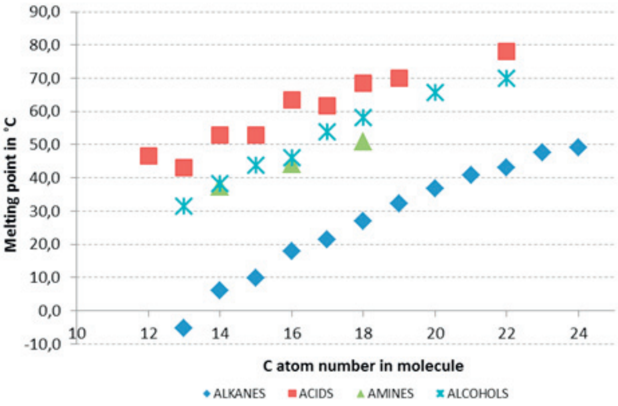

Fig.1: The melting points of alkanes (rhombus), carboxylic acids (square), amines (triangle) and alcohols (star).

The analysis of straight chain alkanes within the range of carbon number 8 – 20 atoms reveals an increase of melting point in proportion to the extension of the chain length, see Figure 1. The same regularity was found in the group of alcohols with the carbon atom number 13 - 18. The longer the chain, the higher is the melting point. This trend was almost linear. From the analysed hydrocarbon derivatives (alkanes, alcohols, acids and amines) the alkanes prove to have the lowest melting points. Generally the melting points of alcohols are lower than melting points of acids, higher than melting points of alkanes and slightly correspond with the melting points of amines in the range of carbon atom number from 14 till 18.

In the analysis of carboxylic acids within the chain length from 12 till 18 was observed the packing effect, as the acids with even carbon atoms have a relatively higher melting point than those of the members with odd numbers. This is due to the crystal structure of the hydrocarbons in the solid state, which differs for the odd and even acids. The even-numbered acids have optimal intermolecular contact at both ends, whereas the odd ones possess these at one end and at the other there is a gap. [11, 12]

The packing effect was not observed in the case of alcohols and could not be estimated in the amine chain, due to lack of odd carbon atom numbered amine samples. So far the increase of the melting point in the direction of tetradecylamine – hexadecylamine – oktadecylamine has been found.

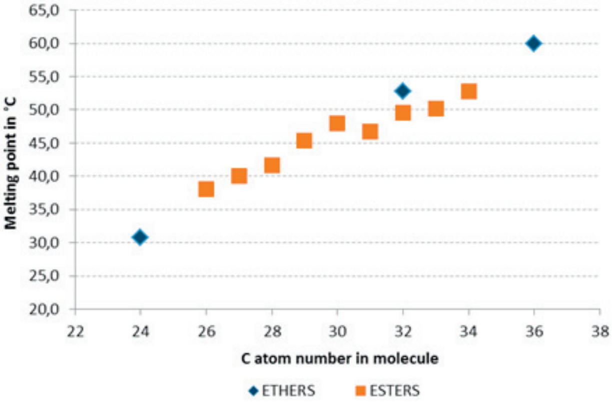

Fig.2: The comparison of melting points of alkanes (rhombus) and esters (square).

Data for ethers were compared and depicted separately in Figure 2 due to their higher number of carbon atoms in the chain. Four samples of ethers were measured, dioctyl ether (m.p. - 8°C, not shown in the figure), didodecyl ether, dihexadecyl ether and dioctadecyl ether. For comparison with the melting points of ethers, the melting points of esters were taken from literature [4]. The melting temperatures of ethers and esters within the carbon atom number range 24 – 36 are slightly similar, which is most likely due to the similar intensity of the intermolecular forces in the crystal lattice of both compounds.

Melting points of dicarboxylic acids did not prove any trend so far, see Figure 3. The melting point values vary strongly in the temperature range of 100 – 180 °C. The analysed carboxylic acids were malonic, succinic, glutaric, adipic, pimelic and sebaccic acid. Azelaic and suberic acid were excluded from this analysis due to their unavailability.

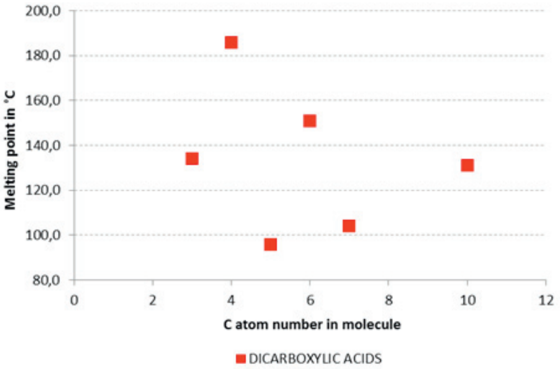

Fig.3: The melting points variation of dicarboxylic acids

3.2. Latent heat of fusion

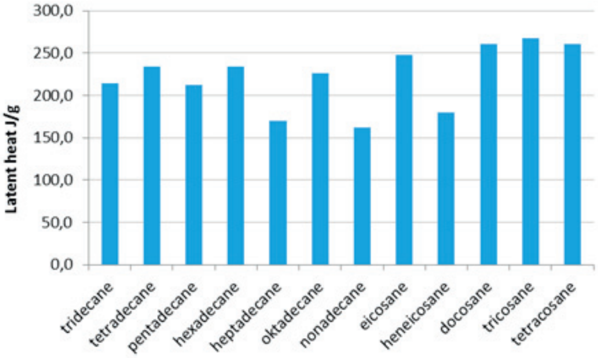

Fig.4: The latent heat of fusion of alkanes with carbon atom number ranged from 13 to 24

As the next step of analysis, latent heats of all mentioned compounds were measured. The latent heat of fusion of alkanes alternate with increasing carbon atom number, see Figure 4. Generally latent heat value of the odd numbered alkane is lower that the latent heat of the alkane with even carbon atom number. The occurrence of more than one crystal form, in other word polymorphism, results in higher latent heat values of the compounds where polymorphism occurred (eicosane, tricosane, tetracosane) than of the compounds where no polymorphism took place (heneicosane). Due to polymorphism two phase transitions take place, first the transition from one solid crystal form to another form; the second transition is from solid to liquid state.

The latent heats of fusion values of carboxylic acids do not show any regularity, as shown in Figure 5. The packing effect, which influence melting point for odd and even numbered carbon chains does not influence the latent heat value. The pentadecanoic, nonadecanoic und docosanoic acidshow the highest latent heat values, above 200 J/g.

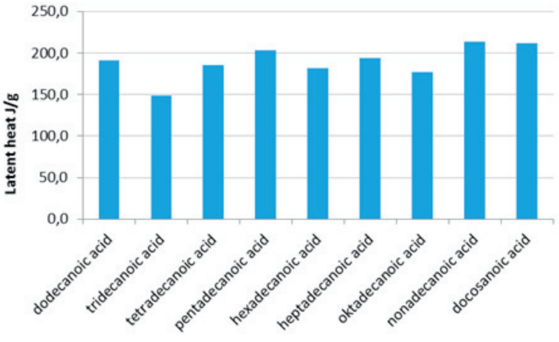

Fig.5: The latent heat of fusion of carboxylic acids with carbon chain length ranged from 12 to 20

Figure 6 depicts the latent heat of fusion of n-alcohols of different chain length and different position of the –OH group. The number of alcohols studied is too small to observe trends dependent on chain length but the effect of the alcohol group is clearly shown. The alcohols with the –OH group attached to the chain in its middlepossess considerably lower latent heat value than the 1-substituted alcohols, with the alcohol group attached at the primary carbon atom.

In Figure 7, the latent heat of fusion of three amines increases with melting point and chain.

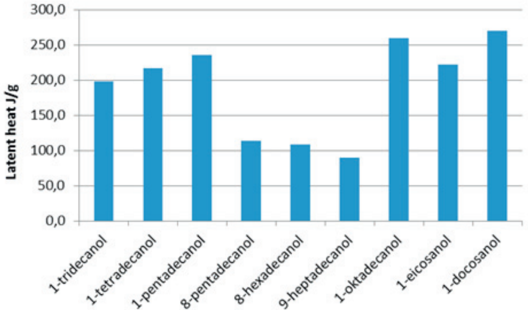

Fig.6: The latent heat of fusion of alcohols with carbon atom number ranged from 13 to 22, with three alcohols with the functional group attached to the hydrocarbon in the middle of the chain.

The ethers possess relatively high latent heat values, but due to the lack of samples (only four samples analysed) it is not possible to obtain any regularity in structure effect, see Figure 8. The highest latent heat was obtained for dihexadecyl (235 J/g) and dioctyl ether (230 J/g). The lowest latent heat value is the one of octadecyl ether (204 J/g).

Carboxylic acids latent heat values varied irregulary, see Figure 9. Adipic acid (219 J/g) possesses the highest latent heat of the analysed compounds, the lowest succinic acid (134 J/g).

Additional to the comparison within functional group thermal characteristics of the same carbon chain length but different functional groups can be studied. For example the derivatives of octadecane (octadecane, octadecanol, octadecanoic acid, octadecylamine) express the following order of increasing latent heat values, carboxylic acid – alkane – alcohol – amine.

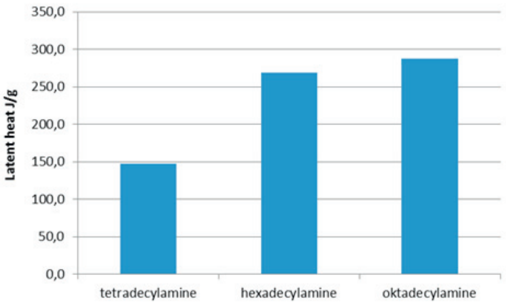

Fig.7: The latent heat of fusion of amines with carbon atom number 14,16 and 18

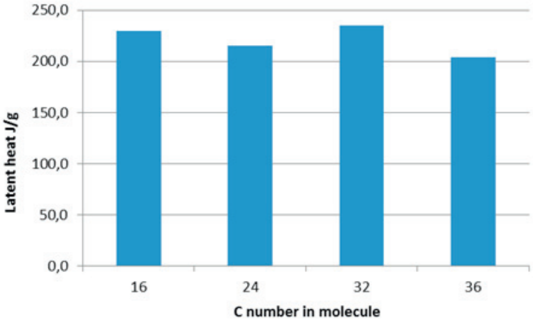

Fig.8: The latent heat of fusion for ethers with carbon atom number ranged from 16, 24, 32 and 36

Additionally following aromatic compounds were analysed, phenol (m.p. 41°C; l.h. 112 J/g), 2-nitrophenol (m.p. 46°C; l.h. 107 J/g), 4-nitrophenol (m.p. 112°C; l.h. 120 J/g), benzoic acid (m.p. 121°C; l.h. 102 J/g), naphthalene (m.p. 80°C; l.h. 108 J/g), 1-naphtol (m.p. 94°C; l.h. 144 J/g), 2-naphtol (m.p. 121°C; l.h. 152 J/g) and 1–napthylamine (m.p. 48°C; l.h. 93 J/g).

Finally the compounds with branched chain and complicated structure were analysed. Pentaglycerine alias 2-(hydroxymethyl)-2-methylpropane-1,3-diol. In the case of pentaglycerine a solid-solid phase change around 80 °C is suitable for storing energy. This is very convenient for many applications, because of the minimum volume change occurring during phase transition from one crystal structure to another and the absence of a resulting in low volatility and simpler requirement regarding the encapsulation. The phase transition at 80 °C is accompanied by a latent heat release of 212 J/g. During analysis of 2-decyl-tetradecanoic acid the melting point of 18°C and the latent heat value of 212 J/g were found.

3.3. Thermal stability and the phase change repeatability

The analysis in open pan in dry air flow could influence the thermal stability of the sample. The cause of the weight loss during analysis can be the evaporation, sublimation or decomposition of the sample. The supercooling can be overestimated due to fast cooling rate 10°C/min.

All the measured alkanes were stable. There was no weight loss/latent heat decrease after 5 cycles. No supercooling of paraffins was observed. Stable thermal behaviour with no supercooling has been proved as well for the alcohols, carboxylic acids and higher amines.

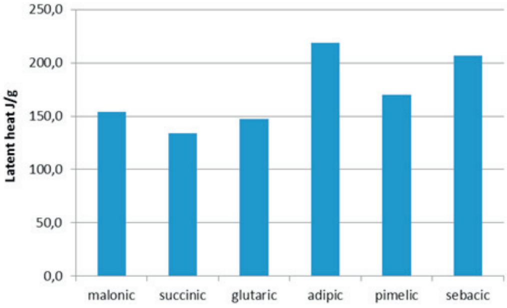

Fig.9: The latent heat of fusion for dicarboxylic acids

An unstable behaviour was found in the analysis of dicarboxylic acids during the open pan system analysis. They tend to supercool, the glutaric acid possessed supercooling of 15°C.

Aromatic compounds showed strong supercooling too. They tend to be volatile and in many cases toxic, which are both undesired properties, since PCMs are supposed to be used in human environment. They showed very unstable behaviour. A few of the latent heat values do not represent the total latent heat as the thermal combustion and weight loss occurred during analysis.

Huge supercooling occurred during the analysis of organic compounds with complicated structure such as pentaglycerine alias 2-(hydroxymethyl)-2-methylpropane-1,3-diol which possesses supercooling of 8°C.

During analysis of 2-decyl-tetradecanoic acid the supercooling was about 15°C. Moreover, the thermal stability of the branched compounds in the open pan was questionable. Compounds with branched chain are suspected of thermal decomposition at higher temperatures.

4. Conclusion

Melting points of n-alkanes with the chain atom number between 13 and 24 and n-alcohols between 13 and 18 carbon atoms increase with the extension of the chain length. Due to lack of amine samples it was not possible to prove this fact for amines. The carboxylic acids with the carbon atom number between 12 and 18 showed the packing effect.

The melting points of dicarboxylic acids with the chain number between 3 and 7 varied strongly and no regularity was found. Even through dicarboxylic acids express desirable characteristics for application (high melting point and high latent heat value) it was found that they are not suitable due to their low thermal stability and combustion during the heating program.

The latent heat of alkanes, alcohols and carboxylic acids were measured but no regularity was found besides the effect of the alcohol group position on the hydrocarbon chain. Position in the middle of the chain significantly lowers the latent heat value of the alcohols, most likely due to the packing effect and lower molecular forces in the molecule.

The higher latent heat values of eicosane, docosane, tricosane and tetracosane are attributed to polymorphism, which was directly observed as more than one phase transition at the temperature range close to the melting point was detected.

Pentaglycerine and 2-decyl-tetradecanoic acid tend to supercool and are unstable, the same as the most of the aromatic hydrocarbons.

In conclusion is this paper collection of experimental thermodynamic data related to the organic phase change materials accompanied by an explanation of several structural effects.

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