MODELLING OF MIXED THERMODYNAMIC MODEL BASED ON NEW MATERIALS

by

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In order to solve the problem of the performance of mixed alkane phase change energy storage materials, this paper proposes the modelling research of mixed thermodynamic model based on new materials. In this paper, the thermodynamic performance of binary mixed alkane system is studied, the influence of phase transition temperature, phase transition enthalpy and its composition on the mixed alkane system is explored, and its solid-liquid phase diagram is drawn. We used different thermodynamic models to predict the phase transition temperature and enthalpy in the melting process of binary mixed alkanes, which were mutually verified with the experimental results. The experimental results show that C9-C10 and C9-C11 systems exhibit eutectic behavior. The eutectic components are 88% (mass fraction, the rest is the same) C9-12% C10 and 90% C9-10% C11. The eutectic temperatures are 218.25 K and 215.15 K, respectively. The C8-C9 system has peritectic phenomenon, C10-C11 system shows complete mutual solubility, and their minimum melting points are 200.25 K and 234.35 K, respectively. Conclusion is that the C9-C10 and C9-C11 eutectic systems are suitable for low temperature phase change materials in the temperature range of 210-220 K, providing data reference for their application in low temperature energy storage.

Key words*: solid liquid phase diagramm, eutectic, advanced new materials, phase change materials, alkanes, thermodynamics, peritectic, molecular thermodynamics*

Introduction

Advanced new materials are materials with excellent performance and special functions that breed strategic emerging industries and lead future scientific and technological development. They are strategic, leading and subversive, and have the technical characteristics of strong industry driving and high added value. The frontier new material industry is a key factor determining the level of high end manufacturing and national defense equipment, and it is of great significance to develop the frontier new material industry. Thermodynamic models (equation of state) and phase equilibrium data are widely used in the fields of petroleum, chemical industry, metallurgy, food, pharmacy*, etc.* In the process industry, and are indispensable basic models and data for process design, simulation, optimization and control modelling [1]. The advantage of thermodynamic model is that it can adapt to a w ide range of temperature and pressure, and describe the behavior of a variety of different substances (small molecules, polymers, electrolytes*, etc.*) and phase states (gas, liquid, solid*, etc.*) at the same time. The thermodynamic model can avoid the selection of the standard state of components between different phase states

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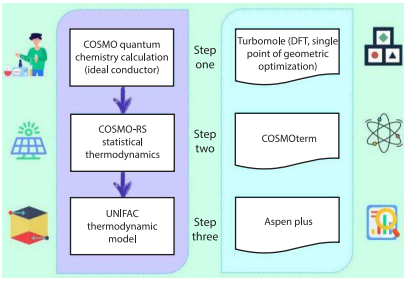

Figure 1. Mixed thermodynamic model

and expand the calculation of the transfer properties of pure fluids and mixtures. The phase equilibrium data is the basis of the model, which can be used to check the adaptability and practicability of the model, and provide reliable data for determining the parameters of the thermodynamic model. Figure 1 shows the mixed thermodynamic model. Under the promotion of industrial policies such as the action plan for cultivating strategic emerging industrial clusters of advanced new materials, China's advanced new materials industry has enjoyed a good momentum of development, but there are major problems such as insufficient original innovation capability, and some key core technologies, key raw and auxiliary materials, core equipment, high end inspection and testing instruments, *etc.* are under the control of others. In the future, it is necessary to carry out a forward-looking top-level design for the development of frontier new material industry, actively give play to the advantages of the new national system, improve the basic capabilities of scientific and technological innovation, support and guarantee, competition and sustainable development of frontier new material industry, and improve the ecological environment of frontier new material industry. In view of the interdisciplinary, innovative and subversive characteristics of frontier new materials, we should cultivate interdisciplinary and innovative industrial talents, fully integrate frontier common key technologies such as material genetic engineering with industrial development, so as to promote the leapfrog development of frontier new materials industry. In order to meet the demand of a new round of scientific and technological revolution and industrial transformation for cutting-edge new materials, this paper puts forward development suggestions from the aspects of material genetic engineering to improve the basic capacity of cutting-edge new materials industry, and the lay-out of cutting-edge new materials industry under the new development pattern of double cycle. At the same time, this paper also puts forward development suggestions on the lay-out of frontier new materials industry under the development strategy of carbon peaking and carbon neutralization, and the construction of independent and controllable frontier new materials testing and characterization capability. Focusing on the testing and evaluation of cutting-edge new materials throughout their life cycle, this paper focuses on breaking through the key common technologies of testing and evaluation of cutting-edge new materials, building more advanced instruments and equipment, deeply studying the methods of analysis and testing, application evaluation, life prediction, failure analysis, *etc.* of cutting-edge new materials, and forming national/industrial standards. We should strengthen the research on comprehensive performance testing of cutting-edge new materials, strengthen talent training and talent introduction, and solve the problems of weak testing and evaluation ability and low level of cutting-edge new materials [2].

Literature review

Alkanes are one of the better phase change energy storage materials. Their mixtures have attracted extensive attention because of their adjustable phase change temperature, stable performance, non-toxic and non-corrosive advantages. Compared with the research on mixed alkanes at medium and normal temperatures, only a few scholars have carried out more systematic research on low temperature mixed alkane systems. Scholars' research on mixed alkane system focuses on the medium and normal temperature (263-323 K). It is rarely reported in the low temperature field, especially below 233 K. The melting point of pure alkane in C_8-C_{11} sys-

tem is between 215-250 K, which meets the temperature demand in the low temperature field. On the other hand, the theoretical prediction of phase transition enthalpy of mixed alkanes is also less. Therefore, in this work, C_8-C_9, C_9-C_{10}, C_9-C_{11}, and C_{10}-C_{11} mixed alkane systems were constructed, thermodynamic characteristics of each mixed alkane system were explored, and phase change point and phase change enthalpy in the melting process were predicted using a variety of thermodynamic models, providing data reference for expanding the application of mixed alkanes in low temperature energy storage systems, such as liquid air energy storage systems and LNG cold energy power generation systems.

Methods

Materials and test methods

Materials

The *n*-octane ($C_8H_{18} \geq 99\%$), *n*-nonane ($C_9H_{20} \geq 99\%$), *n*-decane ($C_{10}H_{22} \geq 98\%$), and *n*-undecane ($C_{11}H_{24} \geq 98\%$) were purchased from Aladdin Company in a certain city.

Test method

Differential scanning calorimetry (NETZSCH, DSC 200F3) was used to measure the thermodynamic properties of mixed alkanes. Each group of samples is cooled and solidified first and then heated and melted at a rate of 5 °C per minute. The N_2 is used for purging during measurement, and the flow rate is 40 mL per minute. The experimental temperature ranges of C_8-C_9, C_9-C_{10}, and C_9-C_{11} systems are –100 °C to –15 °C, –75 °C to –15 °C, and – 90 °C to 0 °C, respectively.

Uncertainty analysis

The uncertainty of temperature and enthalpy measured in the experiment is ±0.1 K. and ±1%, respectively, and the uncertainty of sample mass is 0.01 mg.

Thermodynamic model

In this work, different activity coefficient models (Ideal model, UNIQUAC model, UNIFAC model) are used to predict the melting point in the melting process of C_8-C_9, C_0-C_{10}, C_0-C_{11}, and C_{1n}-C_{11} systems, and the enthalpy prediction model is used to predict the melting enthalpy. The activity coefficient model is based on the phase equilibrium theory to apply the activity coefficient y_i to the prediction of the mixed system of multiple alkanes. Therefore, the expression of complete solid-liquid phase equilibrium of the mixed system is shown:

$$\ln x_i Y_i = \frac{\Delta H_i}{\mathrm{R}T_i}\left(\frac{T_i}{T}-1\right) - \frac{\Delta c_p}{\mathrm{R}}\left(\frac{T_i}{T}-1\right) + \frac{\Delta c_p}{\mathrm{R}}\ln\frac{T_i}{T} \tag{1}$$

Compared with other influencing factors, the smaller specific heat tolerance can usually be ignored. Therefore, the simplified result is shown:

$$\ln x_i Y_i = \frac{\Delta H_i}{\mathrm{R}T_i}\left(\frac{T_i}{T}-1\right) \tag{2}$$

Ideal model

It is assumed that the liquid phase is an ideal solution and the solid phase is a pure or ideal phase in the phase transition process. Therefore, the activity coefficient $y_i = 1$, so eq. (2) is simplified to eq. (3), and X_i is the mass fraction of the main component *i* in the mixture:

$$\ln x_i = \frac{\Delta H_i}{\mathrm{R}T_i}\left(\frac{T_\mathrm{i}}{T} - 1\right) \tag{3}$$

The UNIQUAC model

The UNIQUAC model consists of combination part and residual part. The combination part includes entropy effect, molecular size difference and free volume. The residual part is the mixing enthalpy caused by the interaction of different molecular energies. The model expression is shown:

$$\ln y_i = \ln y_i^{\mathrm{comb}} + \ln y_i^{\mathrm{res}} \tag{4}$$

$$\ln y_i^{\mathrm{comb}} = \ln\left(\frac{\phi_i}{x_i}\right) + 1 - \left(\frac{\phi_i}{x_i}\right) - \frac{Z}{2} q_i \left[\ln\left(\frac{\phi_i}{\theta_i}\right) + 1 - \frac{\phi_i}{\theta_i}\right],\ z = 10 \tag{5}$$

$$\ln \gamma_i^{\mathrm{res}} = q_i \left[1 - \ln\left(\sum_{j=1} \theta_i \tau_{ji}\right) - \left(\sum_{i=1} \frac{\theta_i \tau_{ij}}{\sum_{k=1} \theta_i \tau_{kj}}\right)\right] \tag{6}$$

where ϕ_i and θ_1 are the average volume fraction (partial fraction) and average area fraction of component i, respectively, and τ_j is a binary parameter, which can be calculated:

$$\phi_i = \frac{x_i r_i}{\sum_j^n x_j r_j},\ \theta_i = \frac{x_i q_i}{\sum_j^n x_j q_j},\ \tau_{jij} = \exp\left(-\frac{\lambda_{ji} - \lambda_{ii}}{q_i \mathrm{R}T}\right) \tag{7}$$

$$r_i = 0.1C_i + 0.0672,\ q_i = 0.1C_i + 0.1141 \tag{8}$$

where r_i and q_i are the measurements of molecular van der Waals volume and molecular surface area. The interaction energy of molecular λ_{ii} and λ_{ij} is obtained from the correlation between molecular interaction and macroscopic physical structure. The interaction energy parameter λ_{ii} and λ_{ij} between two different molecules is equal to the λ_{ij} of short chain, j, alkanes in pure alkanes, *i.e.* $\lambda_j = \lambda_{ij} = \lambda_{ij}$. The equation for calculating the interaction energy is shown in eq. (9), where Z is the lattice coordination number and ΔH is the enthalpy of pure alkanes [3]:

$$\lambda_{ii} = -\frac{2}{Z}\left(\Delta H_i - \mathrm{R}T\right),\ \lambda_{ij} = -\frac{2}{Z}\left(\Delta H_j - \mathrm{R}T\right),\ Z = 10 \tag{9}$$

The UNIFAC model

The UNIFAC model changes the activity coefficient algorithm on the basis of UNIQUAC model, and uses the sum of the combined part and residual part in the multi-component mixture to calculate Y_i. For binary mixtures of alkanes, it is assumed that the residual Gibbs free energy of only the mixture is zero, so the residual term is ignored. Therefore, the combination term is used to describe the non-ideality of the mixed system:

$$\ln y_i = \ln\left(\frac{\phi_i}{x_i}\right) + 1 - \left(\frac{\phi_i}{x_i}\right) - \frac{Z}{2} q_i \left[\ln\left(\frac{\phi_i}{\theta_i}\right) + 1 - \left(\frac{\phi_i}{\theta_i}\right)\right],\ Z = 10 \tag{10}$$

where θ_i and ϕ_i are expressed by the equation.

Eutectic model

According to the Second law of thermodynamics and the theory of phase equilibrium, the relationship between the enthalpy of binary mixture at the liquidus is obtained. The calculation equationa of the melting enthalpy of mixed eutectic system:

$$H_m = T_m \sum_{i=1}^{n} \left[\frac{X_i H_i}{T_i} + X_i \left(c_{p,li} - c_{p,si} \right) \ln \frac{T_m}{T_i} \right] \tag{11}$$

When the temperature difference before and after the phase transition is small and the specific heat tolerance of the solid and liquid phase is almost zero, H_m can be simplified:

$$H_m = T_m \sum_{i=1}^{n} \frac{X_i H_i}{T_i} \tag{12}$$

Regularsolution model

In the thermodynamic model, the mixing entropy of phase change materials is assumed to be in the ideal state, and the expression of the corresponding mixing enthalpy is obtained. By simplifying the enthalpy of mixing, the expression is improved according to the empirical formula and the correction coefficient α. The improved expression:

$$H_m = T_m \sum_{i=1}^{n} \alpha x_i \left[\frac{H_{\mathrm{i}}}{T_{\mathrm{i}}} - \mathrm{R} \ln \left(x_i \right) \right] \tag{13}$$

Thermodynamic model prediction

Since the development of thermodynamic models and data, the theoretical structure has become increasingly perfect, and data accumulation has continued to increase, providing a strong guarantee for solving general problems in the fields of process industry operation, material design, energy development*, etc.* In this work, Ideal, UNIQUAC, and UNIFAC models are used to predict the melting temperature, T_m, in the melting process, and Eutectic and Regularsolution models are used to predict the melting enthalpy, H_m, [4].

Results and discussion

Figures 2-4 shows the predicted results and experimental data of melting point and enthalpy of C_8-C_9, C_9-C_{10}, C_9-C_{11}, and C_{10}-C_{11} systems. The relative deviation (RD) and average relative deviation (ARD) are calculated:

$$\mathrm{RD}_{T(H)} = \left| \frac{T(H)_{i,\mathrm{exp}} - T(H)_{i,\ \mathrm{pre}}}{T(H)_{i,\ \mathrm{pre}}} \right| \times 100 \tag{14}$$

$$\mathrm{ARD}_{T(H)} = \left[\frac{1}{m} \sum_{i=1}^{m} \left| \frac{T(H)_{i,\ \mathrm{exp}} - T(H)_{i,\ \mathrm{pre}}}{T(H)_{i,\ \mathrm{pre}}} \right| \right] \times 100 \tag{15}$$

The average relative deviations of T_m and H_m predicted by these models are listed in tab. 1.

As shown in figs. 2(a) and 2(b), the average relative deviations of the melting point predicted by Ideal and UNIFAC models for C_8-C_9 system are 1.45% and 1.34%, respectively. The UNIQUAC model has higher precision, and its average relative deviation is. The melting

enthalpy predicted by the Regularsolution model decreases first and then increases with the increase of C_9 component, with an average relative deviation of 8.68%. The large deviation is caused by multiple phase transformations caused by peritectic reaction [5].

Table 1. Average relative deviation of four binary systems on Ideal, UNIFAC, UNIQUAC, Eutec, and Regularsolution models

Mixed system	Average relative deviation [%]				
	Melting temperature			Melting enthalpy	
	Ideal	UNIQUAC	UNIFAC	Eutectic	Regularsolution
C_8-C_9	1.45	0.91	1.34	14.26	8.68
C_9-C_{10}	1.96	1.79	1.95	15.42	8.54
C_9-C_{11}	1.18	1.20	1.14	12.64	6.70
C_{10}-C_{11}	0.82	1.31	0.80	17.88	9.66

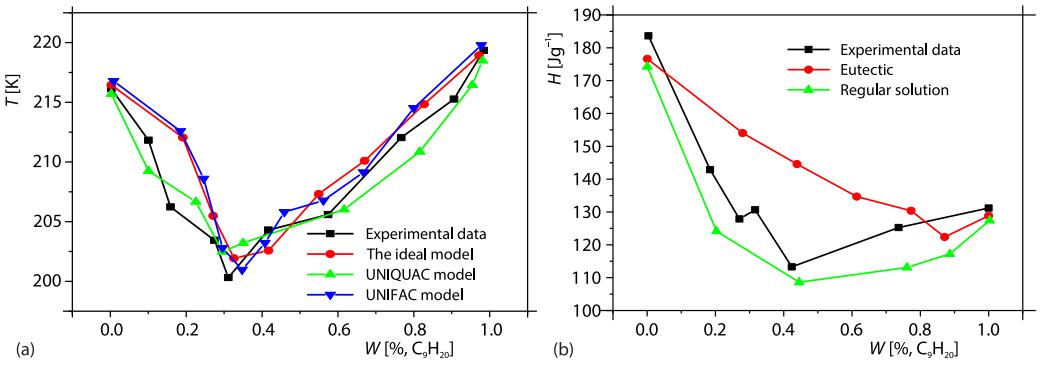

Figure 2. Melting point and enthalpy of C_8-C_9 binary system

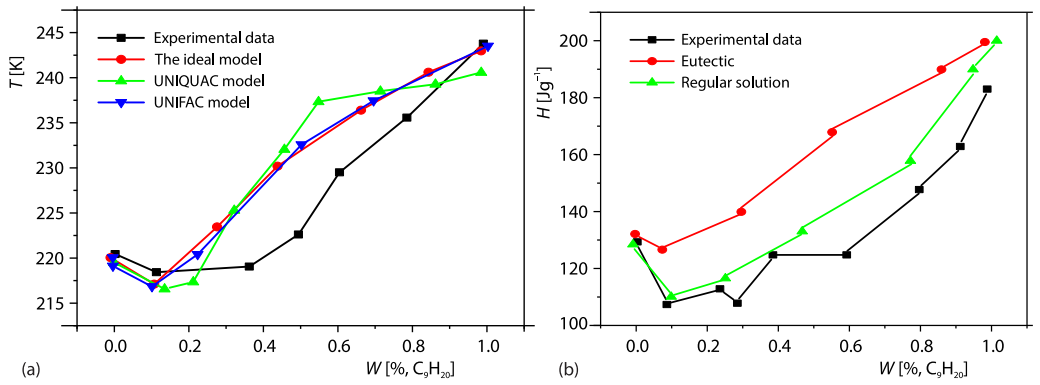

Figure 3.Melting point and enthalpy of C_9-C_{10} binary system

As shown in figs. 3(a) and 3(b), the comparison between the predicted melting point and melting enthalpy of C_9-C_{10} system and the experimental results shows that the average relative deviation of the melting point predicted by Ideal, UNIQUAC, and UNIFAC models is 1.96, 1.79, and 1.95%, respectively, and the Ideal model has the maximum relative deviation of 4.63%. The deviation of melting enthalpy predicted by the Regularsolution model is smaller, and the trend of predicted results is similar to the experimental data, with an average relative deviation of 8.54 [6].

As shown in figs. 4(a) and 4(b), Ideal, UNIQUAC, and UNIFAC models have similar prediction accuracy for the melting point of C_9-C_{11} system, with average relative deviation of 1.18%, 1.20%, and 1.14%. The maximum relative deviations of the predicted results of Ideal and UNIFAC models are 15.23% and 25.18, respectively. The melting enthalpy predicted by the Regularsolution model is more similar to the experimental data, with the maximum relative deviation of 14.80% and the average relative deviation of 6.70%. The predicted results are more referential.

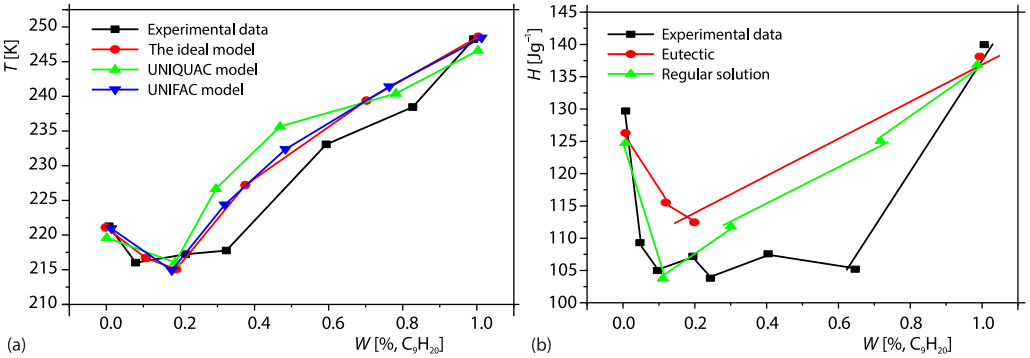

Figure 4. Melting point and enthalpy of C_9-C_{11} binary system

According to the prediction results and experimental data of C_{10}-C_{11} system, UNIFAC model has the highest prediction accuracy for melting point, and the average relative deviation of this model is 0.80%. The average relative deviation of the predicted results of Ideal and UNIQUAC models is 0.82% and 1.31%, respectively, of which the maximum relative deviation of Ideal model is 2.26%. The prediction accuracy of the Regularsolution model for the melting enthalpy is higher, with an average relative deviation of 9.66%, while the average relative deviation of the Eutectic model is 17.88% [7].

The UNIQUAC and UNIFAC models have higher prediction accuracy for the melting temperature of the mixed system. The prediction results of UNIQUAC model for C_8-C_9 and C_9-C_{10} systems are more accurate, and the average relative deviation of UNIQUAC model for C_9-C_{11} and C_{10}-C_{11} systems is smaller. For C_8-C_9 and C_9-C_{11} systems, the curve of the prediction model shows the lowest point near 32%C_9 and 48%C_{11} components, which is consistent with the experimental phase diagram. For C_9-C_{10} and C_9-C_{11} systems, the lowest melting point component of the prediction model is slightly higher than the experimental value and the melting point temperature is lower than the experimental value, because the melting point temperature of pure alkanes C_9 and pure alkanes C_{10} and C_{11} differ greatly. The prediction results using Ideal and UNIFAC models have similar average relative deviation, but the deviation of UNIQUAC model prediction results is not reflected. This is because the residual term is considered in the UNIQUAC model, in which the binary parameter τ_{ji} involves the molecular interaction energy. Due to the existence of weak molecular interaction between eutectic components and the effect of molecular self association, the residual term is sensitive to the prediction results. The Regularsolution model has higher prediction accuracy for the melting enthalpy of four systems, among which the average relative deviation of C_9-C_{11} system is the smallest, 6.70% [8]. For the prediction of the melting enthalpy of the four systems, the average relative deviation of the Eutectic model is large (about 15%), while the average relative deviation of the Regular solution model is small (about 8.4%). This is because in addition the part involving the mixing enthalpy in the Regular solution model, it is assumed that the mixing entropy is in the ideal state. When the model involves the ideal mixing entropy, the deviation of the prediction results

is relatively reduced. Therefore, the Regular solution model is better than the Eutec model in predicting the enthalpy of mixed alkanes. For the enthalpy prediction of most mixed alkanes, the prediction results related to the experimental points can be well obtained. In conclusion, UNIQUAC model and Regularsolution model have higher prediction accuracy for the melting point and melting enthalpy of mixed alkane system, and are suitable for thermodynamic prediction models [9, 10].

Conclusion

In this paper, the modelling research of mixed thermodynamic model based on new materials is proposed. In this work, the thermodynamic properties of C_8-C_9, C_9-C_{10}, C_9-C_{11}, and C_{10}-C_{11} binary alkane low temperature phase change materials are studied experimentally and performance prediction. The main conclusions are UNIQUAC and UNIFAC models have high accuracy in predicting the melting temperature of four binary systems. For C_8-C_9 and C_9-C_{10} systems, UNIQUAC model is more accurate in predicting the melting temperature, and the average relative deviation is and, respectively. For C_9-$C_1$1 and C_{10}-C_{11} systems, the average relative deviation of UNIFAC model is small, which is C_9-C_{10} and C_9-C_{11}, respectively. For the prediction of the melting enthalpy of four systems, the accuracy of the Regular solution model is the highest, and their average relative deviations are and, respectively. To sum up, the four systems and mixed alkanes as eutectic systems are suitable choices for low temperature phase change materials, providing data reference for applications in low temperature energy storage systems (such as liquid air energy storage systems, LNG cold energy power generation systems).

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