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BRIEF COMMUNICATIONS

Study of Fusion Diagrams of Two-Component Systems *n*-Tricozane–Pentadecane and *n*-Tricosane–Hexadecane by Low-Temperature Differential Thermal Analysis

I. P. Kalinina, A. Yu. Kopnina, and I. K. Garkushin

Samara State Technical University, Samara, Russia

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Abstract—The two-component systems *n*-tricozane–pentadecane and *n*-tricozane–hexadecane were studied by low-temperature differential thermal analysis. The characteristics of the eutectic compositions were determined.

To predict and study the phase diagrams, the authors analyzed a number of two-component systems formed by *n*-tricosane and *n*-alkanes and determined the specific enthalpies of fusion of the eutectic compositions.

The main method used in the study was low-temperature differential thermal analysis (LDTA) [1–4]. The heating and cooling curves for the compositions studied were measured on an LDTA installation with a TZ 4620 double-line flat self-recorder. As a source of the thermoelectromotive force served a Chromel–Copel thermocouple, with one of its junctions immersed into the mixture under study and the other placed in a test tube filled with a reference indifferent substance (calcined powdered aluminum oxide). The cold junction of the thermocouple was in a Dewar flask filled with a mixture of water and ice, which had a temperature of 0°C. The thermoelectromotive force of the differential thermocouple was amplified with an F 116/1 photoamplifier. The sensitivity of the differential recording was attenuated with an MSR-33 resistance box. The zero line of the differential curve was shifted with an IRN-64 source of variable voltage. The temperature was determined to within ±0.2°C. The compounds studied were cooled and heated in a TK-1 thermal chamber. The study was performed in the temperature range 233–333 K. The rate of cooling and heating of the compounds was 1–2 deg min^{-1}. The starting components were weighed on a VLR-2000 analytical balance with an accuracy of 0.3 mg. The characteristics of the individual substances corresponded to the reference data [5, 6].

n-Tricosane **I** containing 98 wt % pure substance, *n*-pentadecane **II**, and commercial *n*-hexadecane **III** of pure grade were used in the study. The purity of the reagents was confirmed by liquid-phase chromatography (Tsvet-100 chromatograph, 50-m × 0.25-mm and 25-m × 0.25-mm capillary columns). The evaporator temperature was 623 K. As a solvent of solid hydrocarbons served toluene.

To perform a preliminary theoretical analysis of the **I**–**II** and **I**–**III** systems, we calculated the hypothetical eutectic compositions by Schroeder's equation, which is commonly used to describe ideal systems [7]:

$$\ln X_1 = \frac{-\Delta H_{\text{fus},i}(T_{\text{mel},i} - T_\text{e})}{RT_{\text{mel},i}T_\text{e}}, \qquad (1)$$

where X_i is the mole fraction of *i*th substance in a mixture; $\Delta H_{\text{fus},i}$ the molar enthalpy of fusion of *i*th component (J mol^{-1}); $T_{\text{mel},i}$, the melting point of *i*th substance (K); T_e, the eutectic temperature (K); and R = 8.314 J mol^{-1} K^{-1}, the universal gas constant.

To confirm the accuracy of determination of the experimentally found specific enthalpies of fusion of the systems, they were calculated by formulas [1, 2]

$$\Delta H_{\text{fus,e}} = x_1 \Delta H_{\text{fus},1} + x_2 \Delta H_{\text{fus},2}, \text{ kJ kg}^{-1}, \qquad (2)$$

$$\frac{\Delta H_{\text{fus,e}}}{T_\text{e}} = \frac{x_1 \Delta H_{\text{fus},1}}{T_{\text{mel},1}} + \frac{x_2 \Delta H_{\text{fus},2}}{T_{\text{mel},2}}, \text{ kJ kg}^{-1}, \qquad (3)$$

where x_1 and x_2 denote the composition of the eutectic

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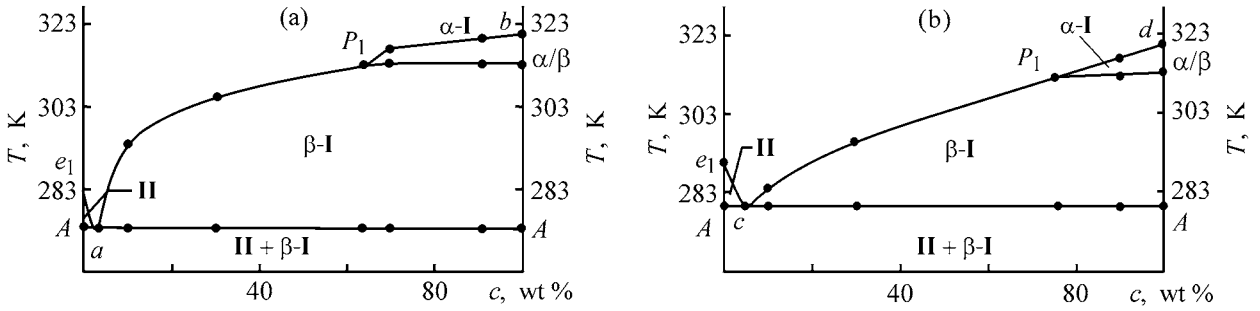

Fig. 1. Phase diagrams of the systems (a) **I**–**II** and (b) **I**–**III**. (T) Melting point of components of the system and (c) content of *n*-alkane. α-**I**, region of crystallization of α-*n*-tricosane; β-**I**, region of crystallization of β-**I**; **II** + β-**I**, region of crystallization of *n*-alkane and β-*n*-tricosane.

(wt %); $\Delta H_{\text{fus},1}$ and $\Delta H_{\text{fus},2}$ are the specific enthalpies of fusion of compounds **I** and **II** [**III**] (kJ kg^{-1}); and $T_{\text{mel},1}$ and $T_{\text{mel},2}$, the melting points of compounds **I** and **II** [**III**] (K).

Table 1. Calculated and experimental eutectic compositions

System	T_{mel}, K	Eutectic composition, mol %	
		$C_{23}H_{48}$	*n*-alkane
I–**II**	273.5	98.0	2.0
		97.9	2.1
I–**III**	279.6	96.5	3.5
		96.7	3.3

* Numerator: experiment, denominator: calculation by Eq. (1).

Table 2. Calculated and experimental specific enthalpies of fusion of eutectic systems

System	Enthalpy of fusion, kJ kg^{-1}/kJ mol^{-1}		
	calculation		experiment, Eq. (4)
	Eq. (2)	Eq. (3)	
I–**II**	163.18/35.05	82.97/21.57	30/24.76
I–**III**	128.00/19.77	83.52/15.43	72/32.44

Table 3. Phase equilibria in the systems **I**–**II** and **I**–**III**

Point (line)	Equilibrium	Phase equilibrium
Eutectic *AaA*	Nonvariant	l ⇄ **II** + β-**I**
Transition P_1	″	l + α-**I** ⇄ β-**I**
e_1a	Monovariant	l ⇄ **II**
aP_1	″	l ⇄ β-**I**
P_1b	″	l ⇄ α-**I**
Eutectic *AcA*	Nonvariant	l ⇄ **III** + β-**I**
Transition P_1	″	l + α-**I** ⇄ β-**I**
e_1c	Monovariant	l ⇄ **II**
cP_1	″	l ⇄ β-**I**
P_1d	″	l ⇄ α-**I**

The experimental enthalpies of fusion of the systems under study were determined using the equation [1]:

$$\Delta H_{\text{fus, e}} = \frac{\Delta H_{\text{fus},1} T_{\text{e}} S m_1}{T_{\text{mel},1} S_1 m}, \quad (4)$$

where ΔH_{fus} is the enthalpy of fusion of the reference substance (*n*-tetradecane), whose melting point is close to that of the eutectic composition (kJ kg^{-1}); T_{mel}, the melting point of the reference substance (K); S_1 and S, the half areas under the peak in the cooling curve of the pure reference substance and a mixture of eutectic composition, respectively (mm^2); m_1 and m, the weighed portions of the pure reference substance and the eutectic mixture, respectively (kg); T_{e}, the melting point of the eutectic composition in the system (K).

The calculated and experimental data obtained are listed in Tables 1 and 2 and shown in Figs. 1a, 1b.

The liquidus curves are represented by three crystallization branches α-**I**, β-**I**, and **II** [**III**]. The minimum crystallization branch corresponds to the compounds **II** [**III**]. The eutectic compositions found experimentally and those calculated by Eq. (1) are listed in Table 1.

The phase equilibria for points and lines of the given diagrams are indicated in Table 3.

CONCLUSION

The phase diagrams of the two-component systems constituted by *n*-tricosane and pentadecane and by *n*-tricosane and hexadecane were studied. The characteristics of their eutectic compositions were determined: mp 273.5 and 279.6 K, eutectic composition 3.0–97 and 5.0–95.0 wt %, and specific enthalpy of fusion 30 and 72 kJ kg^{-1}, respectively.

REFERENCES

1. Kopnina, A.Yu., Agafonov, I.A., Garkushin, I.K., and Miftakhov, T.T., *Trudy respublikanskoi nauchno-tekhnicheskoi konferentsii molodykh uchenykh "Khimicheskie nauki. Khimicheskie tekhnologii"* (Proc. of Republican Sci. and Eng. Conf. of Young Scientists "Chemical Science. Chemical Engineering"), Samara, 1999, p. 14.
2. Kopnina, A.Yu., Agafonov, I.A., Garkushin, I.K., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 2001, vol. 44, no. 5, pp. 84–85.
3. Agafonov, I.A., Garkushin, I.K., and Miftakhov, T.T., *Zh. Fiz. Khim.*, 1999, vol. 73, no. 5, pp. 785–787.
4. Agafonov, I.A., Garkushin, I.K., and Miftakhov, T.T., *Fazovye ravnovesiya v dvukhkomponentnykh sistemakh iz n.-alkanov* (Phase Equilibria in Two-Component Systems of *n*-Alkanes), Samara: Samara Gos. Tech. Univ., 1997.
5. Tatevskii, V.M., *Fiziko-khimicheskie svoistva individual'nykh uglevodorodov* (Physicochemical Properties of Individual Hydrocarbons), Moscow: Gostoptekhizdat, 1959.
6. *Svoistva organicheskikh soedinenii* (Properties of Organic Compounds), Potekhina, A.A., Ed., Leningrad: Khimiya, 1984.
7. Stromberg, A.G. and Semchenko, D.P., *Fizicheskaya khimiya* (Physical Chemistry), Stromberg, A.G., Ed., Moscow: Vysshaya Shkola, 2003.