ELSEVIER

Thermochimica Acta 345 (2000) 25–30

thermochimica acta

www.elsevier.com/locate/tca

Phase transitions in some *n*-alkanes and petroleum waxes — investigation by photoacoustic and exoelectron emission techniques

T. Górecki[a], S.P. Srivastava[b,*], G.B. Tiwari[b], Cz. Górecki[c], A. Żurawska[c]

[a]*Institute of Physics, Opole University, ul. Oleska 48, PL 45-052 Opole, Poland*
[b]*Indian Institute of Petroleum, Dehradun 248 005, India*
[c]*Physics Laboratory, Technical University, ul. Ozimska 75, PL 45-370 Opole, Poland*

Received 26 July 1999; received in revised form 27 October 1999; accepted 1 November 1999

Abstract

The use of the photoacoustic (PA) effect and photostimulated exoelectron emission (EEE) technique in the investigation of first- and second-order phase transitions in pure *n*-alkanes such as *n*-C_{22}, *n*-C_{28} and *n*-C_{32} and in three petroleum waxes having different carbon number distributions, have been examined. Changes in the amplitude and phase of the PA signal with temperature and the temperature dependence of the intensity of photostimulated EEE across the phase transitions have been measured. These measurements have shown that both the polymorphic phase transitions and melting of these hydrocarbons are accompanied by jumps or peaks of the PA amplitude and phase and EEE intensity, thus enabling the detection of the solid–solid and solid–liquid phase transitions. These results are further confirmed by a comparison with those obtained by differential thermal analysis (DTA) control measurements performed at the same heating and/or cooling rate. The PA and EEE results thus obtained are discussed in the light of phase transition temperatures obtained from other techniques. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Petroleum waxes; *n*-Alkanes; Phase transitions; DTA; Photoacoustic; Exoelectron emission

1. Introduction

The importance of the study of phase transition(s) in *n*-alkanes and petroleum waxes lies in the fact that the related parameters have been shown to govern the solubility of these hydrocarbons in organic solvents [1,2], on which depend the industrial applications of these materials. A number of thermal and spectroscopic methods have been then used to understand the changes in the properties at phase transitions, and each method has given its own unique information supplementing/complimenting each other [1]. Although the relatively recent techniques of the photoacoustic effect (PA) and exoemission of electrons (EEE) have been widely used [3–8] to study the temperatures of solid–solid and solid–liquid phase transitions in various compounds, no attempt seems to have been made so far, to our knowledge, to apply these techniques to the study of phase transitions in lamellar hydrocarbons like *n*-alkanes and petroleum waxes. In this work the results of PA and EEE investigations as well as those of a parallel differential thermal analysis (DTA) on these hydrocarbons are presented and the applicability of PA and EEE techniques to the unfold-

---

[*] Corresponding author. Tel.: +91-135-660113; fax: +91-135-671986.
E-mail address: iipddn@del2.vsnl.net.in (S.P. Srivastava).

PII: S0040-6031(99)00398-6

ing of the characteristics of these organic solids at phase transitions is discussed.

2. Experimental

2.1. The samples

2.1.1. n-Alkanes

The *n*-alkane *n*-docosane (n-C_{22}) was procured from Fluka with a stated purity greater than 99.5% by GC and *n*-octacosane (n-C_{28}) and *n*-dotriacontane (n-C_{32}) were procured from Aldrich with a stated purity of more than 99% each. The samples were used as received, without any further purification.

2.1.2. Petroleum waxes

Three petroleum waxes — following the nomenclature of our earlier work [9] — UAN-1 (melting range: 39.0–56.5°C, average chain length: 24.5, carbon number distribution range: n-C_{19}–n-C_{34}), UAN-7 (melting range: 66.2–74.5°C, average chain length: 31.3, carbon number distribution range: n-C_{24}–n-C_{43}) and UAN-8 (melting range: 43.0–62.5°C, average chain length: 28.2, carbon number distribution range: n-C_{20}–n-C_{39}) have been selected for the present study. These waxes are obtained by the urea adduction of the VGO fraction (370–550°C, UAN-8) and its subfractions (370–400°C, UAN-1 and 525–550°C, UAN-7) of Neelam (Indian off-shore) crude oil [9]. The method of preparation and characteristics of these waxes are reported in detail elsewhere [9,10].

2.2. PA measurements

2.2.1. Principle of measurement

The PA effect detects the phase changes in a thin surface layer. The PA signal in a solid is produced by the periodic changes in the sample surface induced by illumination with a light beam of modulated intensity, which causes a pressure fluctuation in the coupling gas (usually air). These pressure fluctuations, which are a function of thermal properties of the sample, are picked up as an acoustic signal by the microphone at the modulation frequency and are analysed as pressure amplitude and phase. At phase transitions the amplitude and phase of the PA signal shows peaks or jumps, thus enabling their detection.

2.2.2. Apparatus

The PA measurements were done using a PA spectrometer (home-built) the details of which have already been reported [3]. The PA excitation was induced by light of periodically modulated intensity emitted by a set of electroluminescence diodes ($\lambda = 665$ nm). To increase the absorption of light by the sample, the material under investigation was mixed with a small amount of carbon black. The sample was optically heated from the backside by means of a halogen lamp. The sample temperature, controlled with a reproducibility of 3 K, was changed at a constant heating rate of 2 K min^{-1}.

2.3. EEE measurements

2.3.1. Principle of measurement and apparatus

The details of the EEE technique and apparatus have already been presented [5,6,11]. To obtain EEE signals for the present samples, an air point counter with a saturated ethanol quenching vapour above the free surface of the liquid was used. During measurements the sample surface was illuminated with unfiltered UV radiation from a quartz lamp with a Q-400 burner. The sample temperature, controlled with a reproducibility of 5 K, was changed at a constant heating (cooling) rate of 10 K min^{-1}.

2.4. DTA measurements

The DTA measurements were performed using a NETZSCH DSC 404/3/F differential scanning calorimeter. The samples were encapsulated in a standard platinum sample pan. An empty pan was used as the reference. A heating/cooling rate of 10 K min^{-1} was used.

All the PA, EEE and DTA measurements were performed in atmosphere of air under normal pressure.

3. Results and discussion

The results of the measurements for *n*-alkanes are shown in Figs. 1–3 for n-C_{22}, n-C_{28} and n-C_{32}, respectively. Likewise, the results on petroleum waxes are presented in Figs. 4–6 for UAN-l, UAN-7 and UAN-8, respectively. In Table 1 the results of phase transition (peak) temperatures obtained by various techniques are compared.

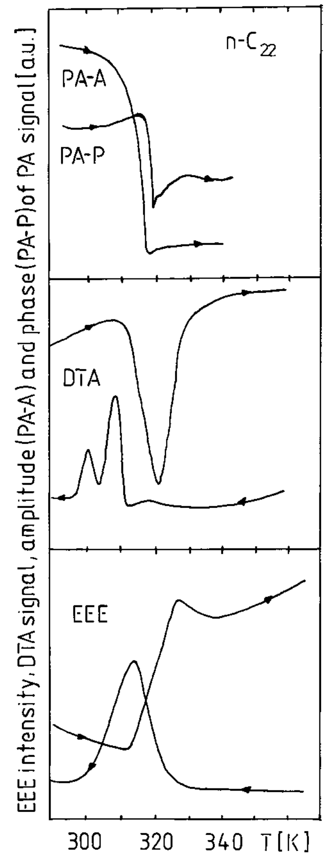

Fig. 1. Temperature dependencies of the photostimulated EEE intensity, DTA signal and the amplitude (PA-A) and phase (PA-P) of the PA signal of *n*-docosane (*n*-C_{22}).

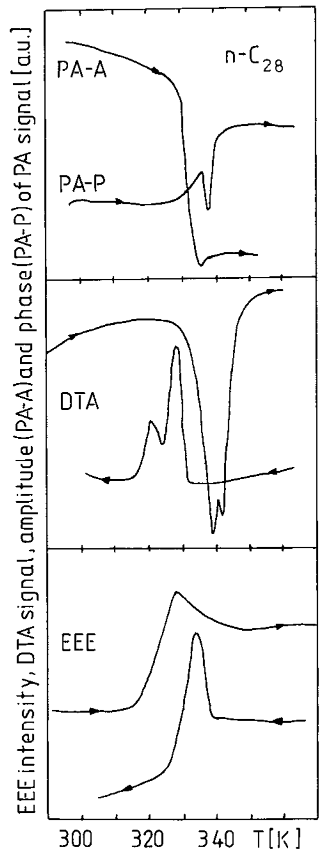

Fig. 2. Temperature dependencies of the photostimulated EEE intensity, DTA signal and the amplitude (PA-A) and phase (PA-P) of the PA signal of *n*-octacosane (*n*-C_{28}).

Table 1
Temperature (K) of the maximum (or minimum) intensity of PA amplitude (PA-A) and phase (PA-P), EEE and DTA signals during phase transition(s) in *n*-alkanes and petroleum waxes

Sample	PA		EEE		DTA		DSC measurements [9,12] for melting
	PA-A melting	PA-P melting	Melting	Solidification	Melting	Solidification	
n-C_{22}	318.0	318.5	319.5	314.5	320.0	317.0 (300.0)	319.3
n-C_{28}	337.5	335.0 (322.0)	326.5	331.5 (329.0)	341.5 (339.0)	326.5 (320.0)	336.3 (332.2)
n-C_{32}	343.0	347.0	345.0	339.0 (326.5)	344.0 (327.5)	331.0 (326.0)	344.1
UAN-1	335.0 (326.5)[a]	338.5	318.5	319.5	330.0 (323.5)	319.5 (315.0)	324.6 (304.7)
UAN-7	341.0	344.5	348.5	338.0	346.5 (339.0)	332.0 (326.0)	344.3 (335.5)
UAN-8	328.0	330.0 (318.0)	333.0	321.0 (306.5)	332.0 (318.0)	313.0 (302.0)	328.4 (312.0)

[a] The values listed in parentheses are the temperatures of solid–solid (second-order) phase transitions.

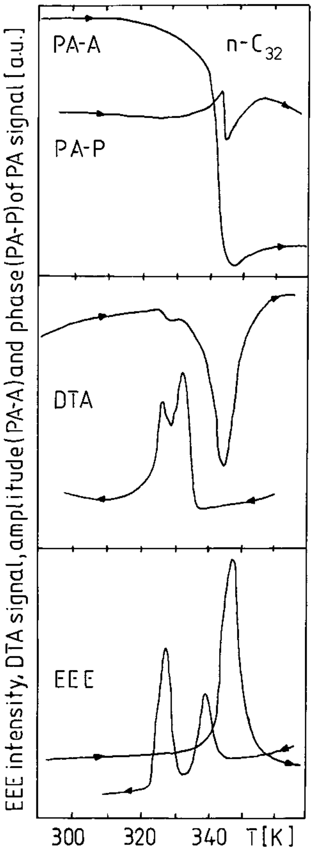

Fig. 3. Temperature dependencies of the photostimulated EEE intensity, DTA signal and the amplitude (PA-A) and phase (PA-P) of the PA signal of n-dotriacontane (n-C_{32}).

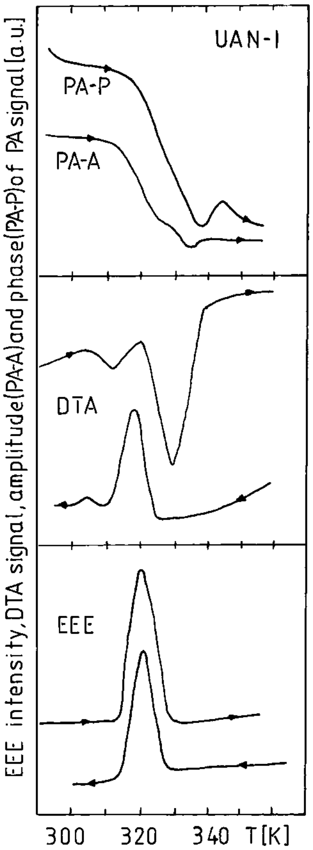

Fig. 4. Temperature dependencies of the photostimulated EEE intensity, DTA signal and the amplitude (PA-A) and phase (PA-P) of the PA signal of the petroleum wax UAN-1 (low average chain length; 24.5).

In this study a higher heating/cooling rate for EEE (10 K min^{-1}) was chosen because it was noticed that the EEE intensity markedly depended on the heating/cooling rate and that the enhancement in the EEE intensity was observable only at the heating/cooling rates of 10 K min^{-1} or greater. In contrast, the clearest PA responses are observed at heating rates smaller than 5 K min^{-1}. It was not possible to perform PA measurements during a cooling cycle.

From Figs. 1–6 it may be observed that the temperature dependencies of PA signals (PA-A (amplitude) and PA-P (phase)) and the intensity of EEE are capable of revealing phase transitions in these organic solids. The curves obtained display peaks or jumps at the phase transition temperatures identical to those observed by DTA. The variation in the intensity with temperature of PA and EEE signals was also found to be sensitive to the structural changes in these solids at the solid–solid phase transition. In general, in case of PA signals the intensities of PA-A and PA-P decrease with temperature near the phase transition, showing minima at the phase transitions. The reverse trend was observed with the EEE intensity. In this case, maxima were observed at the phase transitions.

In cases of both pure n-alkanes and petroleum waxes the results on phase transition temperatures obtained from PA, EEE and DTA techniques agree satisfactorily among themselves (Table 1) as well as with those obtained by differential scanning calorimetry (DSC) earlier [9,12]. For example, in case of n-C_{22}, Fig. 1, the DTA curve contains a peak due to the melting transition and two peaks due to liquid–solid

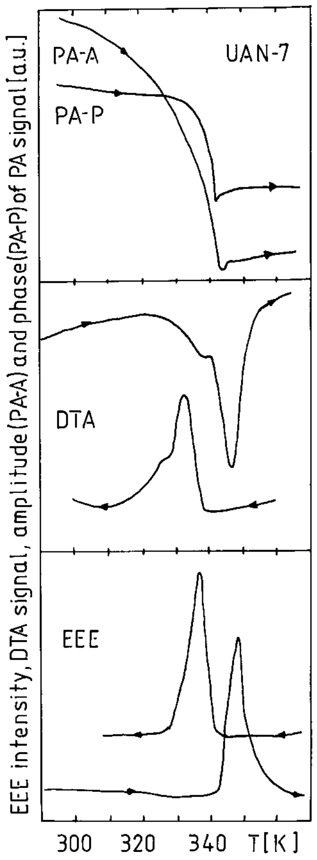

Fig. 5. Temperature dependencies of the photostimulated EEE intensity, DTA signal and the amplitude (PA-A) and phase (PA-P) of the PA signal of the petroleum wax UAN-7 (high average chain length; 31.3).

(317 K) first-order and solid–solid (310 K) second-order transitions. The PA-A and PA-P curves contain melting transition peaks at 317.5 and 318.5 K, respectively. These temperatures are very similar to those obtained from DTA as well as from DSC. The EEE curve obtained during the heating cycle shows both the solid–solid and solid–liquid transitions, the temperatures of which are close to those obtained from DTA. However, the EEE curve obtained during the cooling cycle displays only liquid–solid first-order transition. The trend in changes in the phase transition temperatures with the change in the chain length (as in *n*-alkanes) or in the average chain length (as in petroleum waxes) as observed is correct. The phase transitions shift towards higher temperatures as the chain length or the average chain length increases.

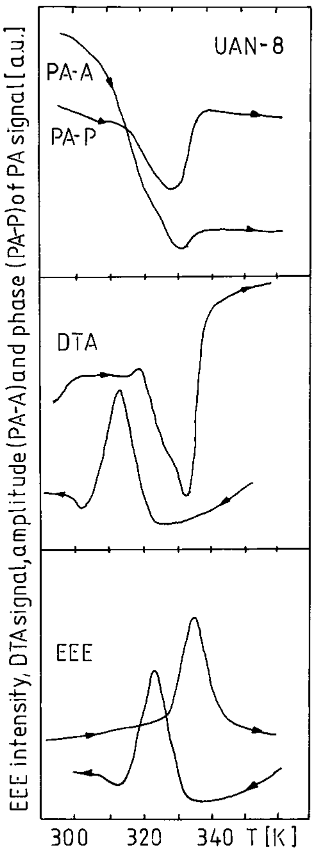

Fig. 6. Temperature dependencies of the photostimulated EEE intensity, DTA signal and the amplitude (PA-A) and phase (PA-P) of the PA signal of the petroleum wax UAN-8 (medium average chain length: 28.2).

4. Conclusions

It may thus be concluded that the techniques of PA and EEE are equally applicable in detecting phase transitions in lamellar hydrocarbons such as *n*-alkanes and petroleum waxes. The phase transition temperatures measured by these techniques are in good agreement with those obtained from other methods. It can be further noted that both the PA and EEE methods detect the phase changes in a thin surface layer of the sample, typically with a thickness of the order of 10 nm in the EEE method, in contrast to the DTA technique which provides information with respect to changes occurring in the bulk of the sample. Since all phase transformations start at the external and internal surfaces of the sample, PA and EEE techniques are most appropriate for such studies. These techniques can be further exploited when samples are available in the form of thin films. The other merits of these two techniques lie in their simplicity, expedition of measurements and ease of sample preparation. It has been further shown [4] that the PA signal at the phase transition, particularly at the second-order phase transition, is related to the specific heat at constant pressure, C_p, of the solid. This suggests the possibility for the establishment of a correlation between phase transition parameters and thermodynamic data using this technique.

Acknowledgements

S.P.S. is thankful to the Opole Technical University, Poland, for providing the financial assistance for his visit to the University during which the experimental work was conceived and initiated. He is also thankful to Dr. T.S.R. Prasada Rao, Director, Indian Institute of Petroleum, Dehradun, for his interest and encouragement in the project.

References

[1] S.P. Srivastava, J. Handoo, K.M. Agrawal, G.C. Joshi, J. Phys. Chem. Solids 54 (1993) 639–670.
[2] S.P. Srivastava, A.K. Saxena, R.S. Tandon, V. Shekhar, Fuel 76 (1997) 625–630.
[3] A. Żurawska, Photoacoustic detection of phase changes in ball-milled selenium, Sci. Rep. Techn. Univ. Opole Phys. 16 (1995) 33–40.
[4] T. Somasundaram, P. Ganguly, C.N.R. Rao, J. Phys. C 19 (1986) 2137–2151.
[5] T. Górecki, B. Sujak, Acta Phys. Polon. A 42 (1972) 487–501.
[6] T. Górecki, Cz. Górecki, L. Biernacki, Thermochim. Acta 130 (1988) 329–334.
[7] Cz. Górecki, T. Górecki, Sci. Rep. Techn. Univ. Opole Phys. 17(220) (1996) 65–72.
[8] T. Górecki, Revista Latinoamericana de Metalurgia y Materiales (Latin Am. J. Metall. Mater.) 7 (1987) 3–17.
[9] G.B. Tiwari, S.P. Srivastava, D.C. Pandey, R.C. Purohit, A.K. Saxena, S.K. Goyal, T.S. Rawat, Petroleum Sci. Technol. 15 (1997) 335–346.
[10] G.B. Tiwari, Studies on wax crystallisation and gel formation in some indigenous crude oils/fractions, Ph. D. Thesis, University of Garhwal, Srinagar, India, 1997 (Chapter III).
[11] B. Sujak, L. Biernacki, T. Górecki, Acta Phys. Polon. 35 (1969) 679–688.
[12] S.P. Srivastava, T. Butz, H.-J. Oschmann, I. Rahimian, Petroleum Sci. Technol. 18 (3–4) (2000), to appear.