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STUDY OF THE EVAPORATION PROCESS USING ISOTHERMAL THERMOGRAVIMETRIC ANALYSIS

BY

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Abstract. Isothermal thermogravimetric analysis (TGA) was used to investigate the evaporation of DDMEBT, an organic compound with third-order nonlinear optical properties. Anthracene was analyzed under identical conditions for comparison. Experiments were conducted at 220–240°C, above the melting points of both compounds. Evaporation rates were determined isothermally, and the Arrhenius equation was applied to obtain kinetic parameters. For DDMEBT, the activation energy was 45.31 kJ/mol and the pre-exponential factor (lnA) was 2.43, with excellent linearity (r^2 = 0.9998). These results indicate evaporation without chemical decomposition and confirm the reliability of the method for low-volatility organic compounds. In the case of anthracene, evaporation was governed by mass transfer, showing Arrhenius behavior and an apparent activation energy of 124.26 kJ/mol, supporting the method’s applicability to polycyclic aromatic hydrocarbons used as reference substances.

Keywords: evaporation, thermogravimetric analysis, DDMEBT, anthracene, activation energy, Arrhenius model.

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1. Introduction

Organic materials exhibiting third-order nonlinear optical (NLO) properties are at the forefront of advanced research in photonics and optoelectronics due to their ability to replace or complement traditional inorganic materials in applications such as optical signal conversion, ultrafast switching, and photonic integration. The growing interest in these materials is justified by their π-conjugated character, donor–acceptor architecture, and remarkable stability under severe thermal and chemical conditions. These features provide a strong and rapid optical response, enabling values approaching the theoretical limits of third-order nonlinear susceptibility (χ^3), as highlighted by Biaggio (2022). An important example within this class is the compound DDMEBT (2-[4-(dimethylamino)phenyl]-3-([4-(dimethylamino)phenyl]ethynyl)buta-1,3-diene-1,1,4,4-tetracarbonitrile), previously characterized by Michinobu *et al.* (2006), Koos *et al.* (2009), and Beels *et al.* (2012). DDMEBT is a small molecule designed based on a rigid tetracyanobutadiene (TCBD) core, functionalized with N,N-dimethylamino groups acting as electron donors and connected via ethynylene bridges that support extended electronic delocalization.

This molecular structure generates a well-defined push–pull system, ensuring high electronic polarizability, relatively low molecular weight, and remarkable thermal stability (Beels *et al.*, 2012; Koos *et al.*, 2009; Michinobu et *al.*, 2006). Previous studies have shown that DDMEBT exhibits moderate volatility and the ability to sublime without chemical degradation up to temperatures of approximately 190°C, where it transitions into the liquid phase, as confirmed by combined TGA-MS-FTIR analyses (Nistor *et al.*, 2025). However, under experimental conditions near its melting point, the compound forms a stable liquid phase, and the characterization of evaporation from this state becomes essential for practical applications involving thermal processing or storage in molten form.

In this context, isothermal thermogravimetric analysis (TGA) emerges as a particularly valuable analytical technique, as it enables real-time monitoring of mass variations of organic compounds at constant temperature, providing essential insights into the mechanisms and kinetics of the evaporation process. Tripodi and Rossetti (2022) demonstrated that TGA, combined with differential scanning calorimetry (DSC), can be successfully employed to determine the energetic parameters of evaporation processes in liquid mixtures without relying on complex thermodynamic models. By correlating mass variation with vapor-phase composition and experimental conditions, the authors were able to estimate apparent enthalpies of vaporization for simple systems using modified Clausius–Clapeyron relationships (Tripodi and Rossetti, 2022). Similarly, the study conducted by Sorokina *et al.* (2002) on cinnamyl alcohol, a liquid aromatic compound, presents a relevant methodological

approach. The authors employed simultaneous thermogravimetric analysis, derivative thermogravimetry, and differential thermal analysis (TGA-DTG-DTA) to determine the kinetic parameters of the evaporation process, including activation energy (66.34 ± 0.84 kJ/mol) and enthalpy of vaporization (68.10 ± 0.84 kJ/mol), highlighting a zero-order kinetic behavior. These results were derived from DTG curves and validated through the application of the Langmuir equation (Sorokina *et al.*, 2002). The methodology applied in this study is further supported by the work of Rong *et al.* (2012), who investigated the evaporation rates of volatile compounds under isothermal TGA conditions, correlating mass loss with vapor pressure using Langmuir- and Antoine-type equations. The authors emphasized the critical role of experimental factors such as crucible geometry, liquid layer thickness, and carrier gas composition, all of which were rigorously controlled in their study (Rong *et al.*, 2012). More recent studies by Fioroni and co-workers (2018, 2019), integrating TGA with DSC and mass spectrometry (MS), have demonstrated that this approach can be extended to determine enthalpies of vaporization even for complex mixtures, such as gasoline–alcohol blends. They reported vaporization enthalpy values of up to 1173.5 kJ/kg (for methanol), highlighting that volatility and mass loss can be accurately quantified under isothermal conditions, even for highly stable compounds (Fioroni *et al.*, 2019). In another study, isothermal thermogravimetric analysis was applied by Moyo *et al.* (2022) to (RS)-5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(trifluoromethylsulfinyl)-1H-pyrazole-3-carbonitrile (fipronil), a compound with low volatility and thermal stability comparable to that of DDMEBT. The authors also demonstrated the feasibility of extracting evaporation kinetic parameters using this method (Moyo *et al.*, 2022).

Based on these theoretical and methodological foundations, the present study aims to investigate, for the first time, the isothermal evaporation behavior of DDMEBT using thermogravimetric analysis to determine the kinetic parameters (E_a and lnA) and evaluate its volatility. This approach provides a new perspective on the use of DDMEBT in optoelectronic applications, where controlled volatility and thermal stability are essential performance requirements. Since anthracene is frequently used as a primary standard for testing equipment dedicated to vapor pressure measurements (Mahnel *et al.*, 2019), it was evaluated under the same experimental conditions as DDMEBT in order to enable a direct comparison of volatility.

2. Materials and Methods

The compound investigated in this study was DDMEBT (2-[(4-dimethylamino)phenyl]-3-[4-((4-dimethylamino)phenyl)ethynyl]-1,3-butadiene-1,1,4,4-tetracarbonitrile), obtained in powder form, with the molecular formula $C_{26}H_{20}N_6$, molecular weight of 416.49 g/mol, and elemental composition of C

74.98%, H 4.84%, and N 20.18% (Nistor *et al.*, 2025). The compound was synthesized at the Department of Materials Science and Engineering, Tokyo Institute of Science, and provided for analysis. Anthracene was used as a reference substance due to its widespread application in thermogravimetric studies (Mahnel *et al.*, 2019). It was tested under identical experimental conditions to assess the validity of the method within the investigated temperature range. Anthracene (≥99% purity) was purchased from Sigma-Aldrich (Merck Group, Darmstadt, Germany) and used without further purification.

DSC curves were recorded using a Mettler Toledo DSC1 instrument at heating rates of 3.5, 5, 10, 15, and 20°C/min over the temperature range 25–250°C. Sample masses ranged between 2.14 and 2.81 mg.

Isothermal TGA measurements were performed using a Mettler Toledo 851^e instrument under an inert nitrogen atmosphere (20 mL/min), with a sample mass of 5.09±0.04 mg. The isothermal curves were recorded at three temperatures: 220°C, 230°C, and 240°C. Heating was conducted at 10°C/min, followed by an isothermal hold for 60 minutes. TGA and DSC data were processed using STAR^e software (v9.1). The kinetic parameters of evaporation were determined based on the Arrhenius equation using the linear representation ln(dm/dt) versus 1/T. The activation energy was calculated from the slope of the linear regression, while the pre-exponential factor (lnA) was obtained from the intercept. The correlation coefficient (r^2) was used to evaluate the consistency of the experimental data. Reported values represent averages from three independent measurements at each temperature.

3. Results and discussions

3.1. Thermal Behavior of DDMEBT Investigated by DSC

To assess the thermal behavior of DDMEBT and identify thermal transitions preceding evaporation or degradation processes, differential scanning calorimetry (DSC) analyses were performed at various heating rates. The DSC curves (Fig. 1) indicate that no detectable thermal transitions occur below approximately 190°C, suggesting good thermal stability within this temperature range. Near this temperature, a pronounced endothermic peak appears, corresponding to the melting process. Immediately after melting, an intense exothermic effect is observed in the temperature range 200–215°C, becoming more pronounced with increasing heating rate. The shift of the peak temperature toward higher values at higher heating rates indicates a kinetically controlled process. This behavior suggests that, following melting, structural reorganization of the molecular system occurs, possibly associated with thermally induced cyclization processes or the formation of supramolecular structures stabilized by π–π interactions between conjugated molecular

fragments. Such transformations are commonly observed in organic compounds with extended π-systems. Furthermore, the increase in peak intensity and the shift of characteristic temperatures with increasing heating rate indicate that the observed processes depend on both temperature and residence time within the respective temperature range. These findings suggest that the thermal transformations occurring near the melting point involve complex processes characterized by significant energy barriers. Given the temperature-dependent nature of these transformations, a detailed kinetic study of the evaporation process at 220, 230, and 240°C is necessary to elucidate the underlying mechanisms and determine the corresponding kinetic parameters.

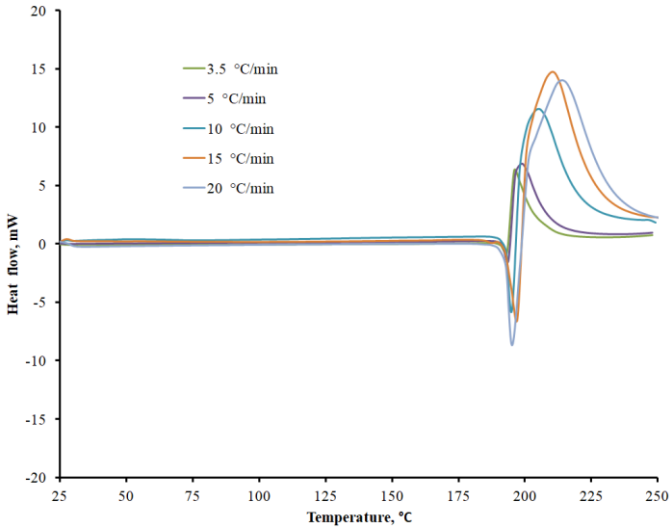


Fig. 1 − DSC curves recorded at different heating rates.

According to literature data, the melting point of anthracene is 216°C (Ye *et al.*, 2018), confirming that the selected temperature range (220–240°C) is appropriate for investigating evaporation processes in both compounds.

3.2. Kinetics of Isothermal Evaporation

The isothermal evaporation of DDMEBT and anthracene was monitored by thermogravimetric analysis under an inert atmosphere at three temperatures: 220°C, 230°C, and 240°C. The evolution of percentage mass loss over time is presented in Figs. 2a and b. In the case of DDMEBT, a gradual decrease in mass is observed, with evaporation rates increasing with temperature, reflecting the thermally activated nature of the process. At 240°C, mass loss occurs significantly faster compared to 220°C, and the observed

behavior is consistent with the kinetics of evaporation processes and their endothermic character. For anthracene, the evaporation rate is significantly higher, with the percentage mass loss approaching 100% after approximately 720 s at 220°C, 468 s at 230°C, and 216 s at 240°C, confirming its high volatility within the investigated temperature range. In this temperature interval, anthracene is in the liquid phase, given its melting point of 216°C; therefore, the observed process is attributed to evaporation from the liquid state. For all investigated temperatures, mass loss varies almost linearly with time over a substantial fraction of the volatilization process. This behavior indicates an approximately constant evaporation rate, suggesting that the process is predominantly controlled by mass transfer at the liquid–vapor interface, without significant limitations imposed by bulk diffusion or structural changes within the sample. An increase in temperature leads to a pronounced acceleration of mass loss, with the slopes of the curves increasing systematically in the order 220°C < 230°C < 240°C. This dependence is characteristic of a thermally activated process and is consistent with an Arrhenius-type description of the evaporation rate. The absence of discontinuities or regime changes in the mass loss curves suggests that, under the experimental conditions employed, thermal degradation or secondary reactions do not significantly contribute to the observed mass loss. The inert atmosphere and the absence of solid residue after the experiment further support the conclusion that mass loss is exclusively due to evaporation. In the literature, experimental data on anthracene evaporation are scarce and often affected by uncertainties, due to the narrow stability range of the liquid phase and its very low vapor pressure. The results presented in this study demonstrate that isothermal thermogravimetric analysis can provide reproducible quantitative information on the evaporation of anthracene in the liquid phase, offering a viable experimental alternative for characterizing this process. As previously noted, data on anthracene evaporation are extremely limited in the literature and considerably more uncertain than those related to sublimation (Mahnel *et al.*, 2019). Therefore, for the determination of the vapor pressure of DDMEBT, the use of an alternative reference substance should be considered.

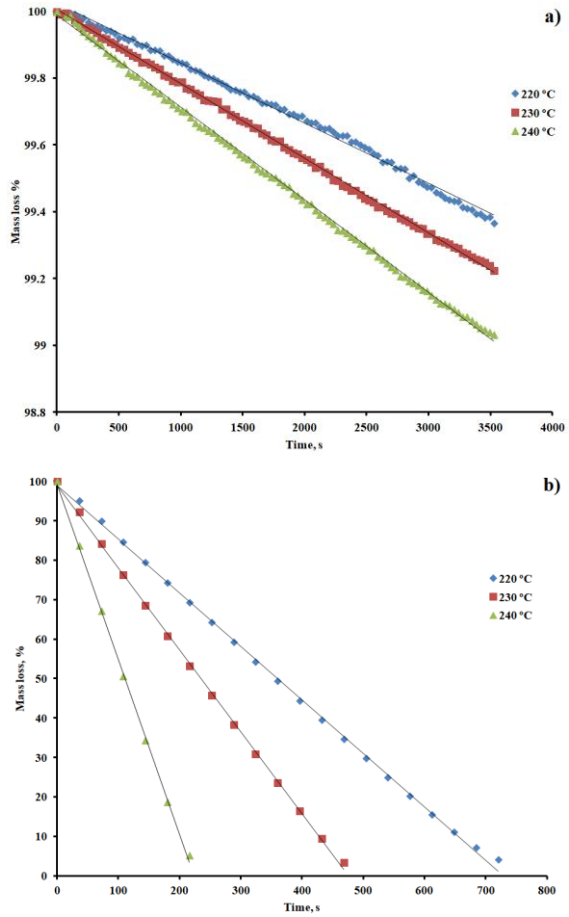


Fig. 2 − Percentage mass loss as a function of time for the evaporation of DDMEBT (a) and anthracene (b) at different temperatures: 220, 230, and 240°C.

Taking into account the amount of evaporated sample and the crucible surface area (0.000019635 m^2), the evaporation rates were calculated at the different temperatures at which the experimental measurements were performed, expressed in $kg/m^2 \cdot s$. Figure 3a and b illustrate the variation of the evaporation rate as a function of temperature for DDMEBT and anthracene. For DDMEBT, a significant increase in the evaporation rate is observed, from approximately $\sim 3 \cdot 10^{-7}$ $kg/m^2 \cdot s$ at 220°C to $\sim 7 \cdot 10^{-7}$ $kg/m^2 \cdot s$ at 240°C. This doubling of the evaporation rate over a 20°C interval supports the hypothesis that molecular kinetic energy becomes sufficient to overcome intermolecular interactions, thereby facilitating the transition to the vapor phase. In the case of anthracene, the evaporation rate increases from approximately $\sim 2.4 \cdot 10^{-2}$ $kg/ m^2 \cdot s$ at 220°C to $\sim 3.4 \cdot 10^{-2}$ $kg/ m^2 \cdot s$ at 240°C.

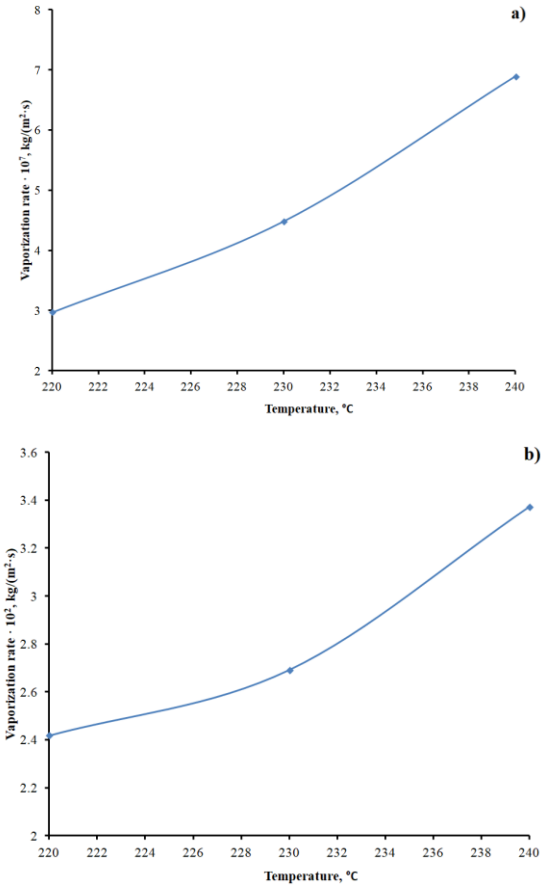


Fig. 3 − Variation of the evaporation rate as a function of temperature for DDMEBT (a) and anthracene (b).

At constant temperature, the evaporation rate remains constant and can be correlated with mass loss according to the following equation:

$$r_{vap} = -dm/dt = k \quad (1)$$

The temperature dependence of the evaporation rate constant can be described by an Arrhenius-type equation:

$$k = Ae^{-Ea/RT} \quad (2)$$

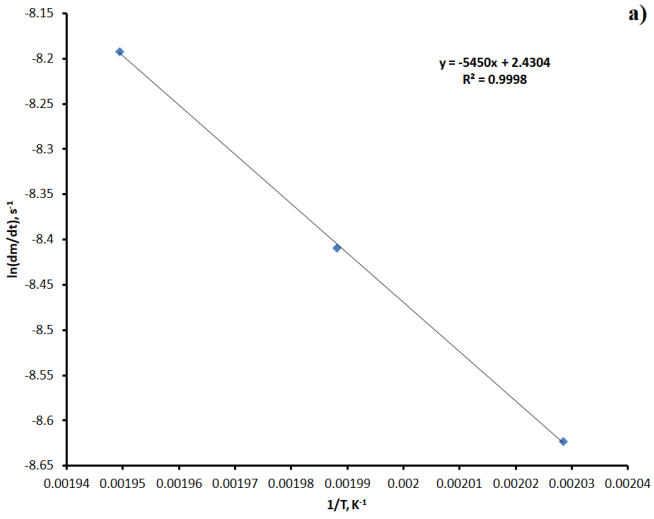
where A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant, and T is the absolute temperature (K).

The evaporation kinetics of DDMEBT and anthracene were evaluated using the logarithmic form of the Arrhenius equation:

$$ln(dm/dt) = lnA - Ea/RT \quad (3)$$

where *dm/dt* represents the evaporation rate constant.

The Arrhenius representation of the evaporation process is shown in Figs. 4a and b, where the natural logarithm of the evaporation rate (ln(dm/dt)) is plotted as a function of the reciprocal absolute temperature (1/T). The regression line obtained for DDMEBT exhibits a negative slope (−5450) and a coefficient of determination r^2= 0.9998, indicating an excellent correlation and confirming the applicability of the Arrhenius law for this system. Based on these data, the activation energy (E_a) was calculated to be 45.31 kJ/mol, while lnA = 2.43 (Table 1). The obtained activation energy confirms an evaporation process controlled by the liquid–vapor interface. Evaporation is fundamentally a surface phenomenon governed by the transition of molecules from the liquid phase to the vapor phase at the interface, with local molecular dynamics controlling the mass flux across this boundary. Recent studies have shown that, under kinetically limited evaporation regimes, resistance in the vicinity of the liquid–vapor interface dominates the evaporation rate and can be described using models that unify molecular-level kinetics (Lu *et al.*, 2019). In TGA experiments, as matter transitions from the liquid to the vapor phase, the release of molecules from the liquid surface is analogous to processes studied at the fluidic or molecular scale. Therefore, the experimentally determined apparent activation energy may reflect not only bulk thermodynamic properties but also the intermolecular interactions that must be overcome at the interface.



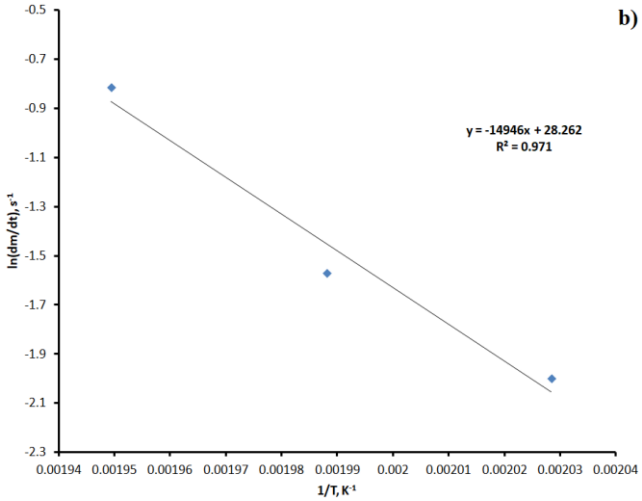


Fig. 4 − Determination of Arrhenius parameters for DDMEBT (a) and anthracene (b).

Table 1

Kinetic parameters derived from the Arrhenius equation

Substance	DDMEBT	Anthracene
Ea, kJ/mol	45.31	124.26
lnA	2.43	28.26
r^2	0.9998	0.9710

These values indicate that, for DDMEBT, the evaporation process is characterized by a moderate energy barrier, typical of compounds with low volatility but high thermal stability. Furthermore, the relatively low value of lnA reflects a reasonable frequency of molecular events favorable to evaporation, consistent with the ordered nature of the phase transition.

The isothermal evaporation of anthracene was investigated by thermogravimetric analysis in the temperature range of 220–240°C, corresponding to its liquid phase. The mass loss exhibited an approximately linear variation with time, indicating a stable evaporation regime. The evaporation rates increased systematically with temperature and followed an Arrhenius-type dependence, from which an apparent activation energy of approximately 124 kJ/mol was determined. This value, which is higher than the enthalpy of sublimation or evaporation reported in the literature (Cochran *et al.*, 2016; Goldfarb and Suuberg, 2008; Mahnel *et al.*, 2019), highlights that the process measured by TGA is a global one, encompassing both the energetic contribution of evaporation and mass transfer effects. These results demonstrate that isothermal thermogravimetric analysis represents a viable method for characterizing the evaporation of anthracene and other low-volatility polycyclic aromatic hydrocarbons (PAHs).

4. Conclusions

In this study, the isothermal evaporation behavior of DDMEBT, an organic material with potential applications in nonlinear optics, was investigated for the first time. Thermogravimetric analysis performed at three temperatures (220°C, 230°C, and 240°C) under an inert atmosphere enabled the determination of the activation energy of the evaporation process (E_a = 45.31 kJ/mol) as well as the pre-exponential factor (lnA = 2.43), confirming a kinetic evaporation regime characteristic of compounds with low volatility and high thermal stability. These results highlight the relevance of applying isothermal methodologies for the kinetic characterization of evaporation processes without the need for external calibration, provided that the investigated compound is thermally well characterized and does not undergo chemical degradation within the analyzed temperature range. DDMEBT thus proves to be a suitable model compound for exploring the volatilization behavior of nonlinear optical (NLO) organic materials under controlled conditions, with potential for extending this approach to other similar compounds. This study contributes to the expansion of the thermal property database for this class of materials and supports the validity of kinetic approaches based on isothermal TGA analysis in the absence of a well-established reference substance. Furthermore, the isothermal thermogravimetric analysis of anthracene in the temperature range 220–240°C revealed a stable evaporation regime predominantly controlled by mass transfer at the liquid–vapor interface, exhibiting Arrhenius-type behavior and an apparent activation energy of approximately 124 kJ/mol. These findings confirm the global nature of the process and suggest that this method can be reliably applied for the characterization of the evaporation of low-volatility polycyclic aromatic hydrocarbons (PAHs), as well as for the selection of suitable reference substances in thermodynamic measurements such as vapor pressure determination.

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STUDIUL PROCESULUI DE EVAPORARE UTILIZÂND ANALIZA TERMOGRAVIMETRICĂ IZOTERMĂ

(Rezumat)

Analiza termogravimetrică izotermă (TGA) a fost utilizată pentru a investiga evaporarea DDMEBT, un compus organic cu proprietăți optice neliniare de ordinul trei. Antracenul a fost analizat pentru comparație în condiții identice. Experimentele au fost efectuate la 220–240ºC, peste punctele de topire ale ambilor compuși. Vitezele de evaporare au fost determinate în condiții izoterme, iar ecuația Arrhenius a fost aplicată pentru a obține parametrii cinetici. Pentru DDMEBT, energia de activare a fost de 45,31 kJ/mol, iar factorul pre-exponențial (lnA) a fost 2,43, cu un coeficient de corelație foarte bun (r^2 = 0,9998). Aceste rezultate indică evaporarea fără descompunere chimică și confirmă fiabilitatea metodei pentru compușii organici cu volatilitate redusă. În cazul antracenului, evaporarea a fost guvernată de transferul de masă, prezentând un comportament Arrhenius și o energie de activare aparentă de 124,26 kJ/mol, susținând aplicabilitatea metodei pentru hidrocarburile aromatice policiclice utilizate ca substanțe de referință.