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CONTRIBUTION OF THERMAL ANALYSIS TO THE DESCRIPTION OF TRANSPORT PHENOMENA OF PESTICIDES
Vaporization enthalpies of two acetanilide pesticides

S. Vecchio[*]

Dipartimento di Ingegneria Chimica, dei Materiali, delle Materie prime e Metallurgia, Università di Roma 'La Sapienza'
Via del Castro Laurenziano 7, 00161 Roma, Italy

The vaporization enthalpies of two acetanilide pesticides, alachlor (2',6'-diethyl-N-(methoxymethyl)-2-chloroacetanilide) and metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-[(1*S*)-2-methoxy-1-methylethyl] acetamide), were determined by processing non-isothermal thermogravimetry data according to the Clausius-Clapeyron equation. The reliability of the procedure proposed was tested carrying out some experiments at different heating rates using acetanilide as a reference compound. A good agreement is found among the vaporization enthalpies derived from all the multi-heating rate experiments as well as with the one predicted from the vapor pressure data taken from literature. The vaporization temperatures (T_{vap}=470±2 K and T_{vap}=479±2 K) and enthalpies ($\Delta_{vap}H°$(436 K)=85±1 kJ mol^{-1} and $\Delta_{vap}H°$(436 K)=70±1 kJ mol^{-1}) for alachlor and metolachlor, were selected, respectively.

Keywords: *acetanilide pesticides, alachlor, Clausius-Clapeyron equation, metolachlor, thermogravimetry, vaporization enthalpy*

Introduction

In the last decades, the use of pesticides increased rapidly all over the world, especially in developing countries. After pesticides were applied to crops undergo transformation under the influence of environment. The persistent agrochemicals often cause health hazards to organisms including animals and man. Their fate when applied to soil and vegetation is largely controlled by several processes such as adsorption, herbicide transformation and transportation in addition to the influence of factors like climatic conditions [1, 2]. Temperature and moisture content of soil are the two factors most related to herbicide persistence [3]. The knowledge of the thermal behaviour and of relevant physico-chemical properties of pesticides is of fundamental importance for the assessment of the environmental fate of pesticides and behaviour of environmental contaminants. Moreover, evaporation of pesticides represents an important contribution to transport phenomena, since they can easily migrate through the atmosphere. In the past, these vaporization characteristics of pesticides were extensively studied using thermal analysis techniques [4–12]. In previous studies, vapor pressures and standard sublimation enthalpies of several pesticides were determined using the TG technique under both non-isothermal and isothermal conditions [13, 14].

On the other hand, TG provides insight into the behavior of substances during changes of temperature. Together with conventional torsion or weighing effusion methods under high vacuum condition [15], TG is applied for vapor pressure and enthalpy measurements of different classes of substances in the presence of a purge gas [6–8, 16–20]. In all these studies a linear relationship between the rate of vaporization and the vapor pressures *P* at a constant gas flow rate is found using Langmuir equation [21]. Moreover, Pieterse and Focke [22] questioned the use of Langmuir expression for describing evaporation at finite pressures into a flowing gas stream because of its diffusion-limited nature. However, Focke [23] proposed a modified vaporization equation when the evaporation of a compound A is limited by diffusion an inert gas B:

$$\mathrm{d}m_\mathrm{A}/\mathrm{d}t=(M_\mathrm{A}AP_\mathrm{A}D_\mathrm{AB})(zRT)^{-1} \tag{1}$$

where z (in mm) is the diffusion path length, D_AB (in m^2 s^{-1}) is the diffusion coefficient.

However, such characteristics can be also obtained more easily by processing non-isothermal thermogravimetry (TG) data according to the Clausius-Clapeyron equation, which can take the form:

$$\ln\alpha=\ln(P/P°)= (\Delta_\mathrm{vap}H°/R)(T_\mathrm{vap})^{-1}-(\Delta_\mathrm{vap}H°/R)(T)^{-1} \tag{2}$$

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[*] stefano.vecchio@uniroma1.it

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

where $\Delta_{vap}H°$ is the standard enthalpy of volatilization, α is the extent of vaporization (equal to $P/P°$), P is the equilibrium vapor pressure at temperature T, $P°$ is the standard (atmospheric) pressure corresponding to the vaporization temperature (T_{vap}), and R is the gas constant [6, 7]. If it is assumed that at any given temperature (T) equilibrium is attained, α can be derived directly from non-isothermal TG curves through the relation: $\alpha=(w_t–w_i)/(w_f–w_i)$, where w_t, is the percentage of mass loss at time t, w_f and w_i are the final and initial percentage of mass loss. Without this assumption $\Delta_{vap}H°$ cannot be determined, since the Clausius-Clapeyron equation corresponds only to equilibrium conditions.

However, diffusion cannot be neglected when a substance evaporates under the conditions in which a TG equipment is used [22, 23]. Moreover, this technique has potentially significant advantages compared to the classical effusion methods the present study aims at obtaining reliable vapor pressure and vaporization enthalpy data on pesticides and to test if one of the proposed TG methods is suitable to this end. As a follow-up of these mentioned studies in the present paper the attention was focused on two acetanilide pesticides, alachlor (2',6'-diethyl-N-(methoxymethyl)-2-chloroacetanilide) and metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-[(1*S*)-2-methoxy-1-methylethyl] acetamide), whose thermal behavior and kinetic characteristics were already discussed elsewhere [24]. The suitability of each TG method proposed was tested using acetanilide as reference compound, since its temperature dependence of vapor pressure is known in a wide temperature range [25].

Experimental

Alachlor (CAS: 15972-60-8) and metolachlor (CAS: 87392-12-9) were supplied by Poliscience, while acetanilide was supplied by Sigma-Aldrich. The suppliers certified that the purity of all the examined herbicides is over 99%. However, all the compounds investigated were purified by simple sublimation. Sample sizes of about 4–6 mg were used for reference and tested compounds.

The simultaneous TG and DSC measurements were carried out in triplicate on a Stanton-Redcroft 625 simultaneous TG/DSC connected to a 386 IBM-compatible personal computer at 1.0 K min^{-1} from ambient to 523 K. The experimental data were collected at every 1 K to give accuracy to the results. The temperature and enthalpy calibration was performed using very pure standards (indium and lead in the present study) whose melting temperature and enthalpies are known [26], while the temperature uncertainty was estimated to be ±0.2 K in all the TG experiments. The DSC curves were used to determine the melting enthalpies from the area of the corresponding endothermic DSC peaks. Argon was used as purge gas with flow rates of 0.83 and 1.33 cm^3 s^{-1}, respectively below and above the open pans. Acetanilide was submitted to supplementary TG experiments at 2.5, 5 and 10 K min^{-1} using identical operating conditions.

Results and discussion

From the first derivative order of experimental TG data for acetanilide the corresponding experimental mass loss rates were determined. In order to obtain the theoretically predicted mass loss rates (Eq. (1)) the diffusion coefficients were calculated using the Fuller's method [27] and the vapor pressure data were taken from [25]. To this end, using the fitting parameters for acetanilide, the following temperature dependence of vapor pressure has been established:

$$\log(P/\mathrm{kPa}) = -30.42 - 3417.2T^{-1} + 17.932\log T - \\ -0.024444T + 8.82\cdot 10^{-6}T^{-2} \qquad (3)$$

over the temperature range from 387 to 825 K. The experimental and the predicted mass loss rates are reported and compared in Table 1. Predicted values exceed always the experimental ones (from 6 to 10%). In particular, at low temperature the values agree satisfactorily, while at higher temperatures a significant disagreement is shown, probably ascribable to diffusion phenomena [22, 23]. As a confirmation of previous studies [22, 23], it can be confirmed that when the mass transport is limited by diffusion through a stagnant gas the TG mass loss rates cannot be used to determine vapor pressure and enthalpy data by means of the Langmuir expression without the knowledge of the temperature dependence of the diffusion coefficient.

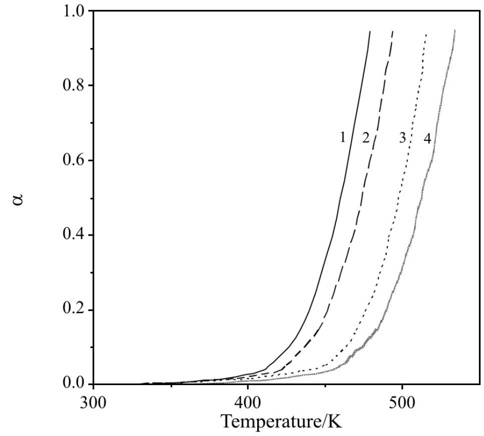

Fig. 1 α *vs.* T plot for acetanilide at 1 – 1 K min^{-1}, 2 – 2.5 K min^{-1}, 3 – 5 K min^{-1} and 4 – 10 K min^{-1}

Table 1 The mass loss for vaporization of acetanilide in a flowing argon atmosphere

T/K	$D_{AB}/10^6$ m^2 s^{-1}	dm/dt/μg s^{-1}		
		Experimental[a]	Predicted[b]	Error/%[c]
401	10.38	2.95	3.14	6.4
403	10.47	2.99	3.19	6.7
405	10.56	3.33	3.55	6.7
407	10.66	3.68	3.93	6.8
409	10.74	4.03	4.31	7.0
411	10.84	4.43	4.75	7.1
413	10.93	4.85	5.20	7.2
415	11.02	5.30	5.70	7.5
417	11.12	5.79	6.23	7.6
419	11.20	6.29	6.78	7.8
421	11.31	6.82	7.36	7.9
423	11.40	7.42	8.01	7.9
425	11.49	8.05	8.70	8.1
427	11.59	8.62	9.33	8.2
429	11.68	9.40	10.19	8.4
431	11.77	10.01	10.87	8.6
433	11.87	10.76	11.68	8.6
435	11.97	11.49	12.49	8.7
437	12.06	12.30	13.37	8.7
439	12.16	13.19	14.36	8.8
441	12.26	13.97	15.21	8.9
443	12.35	14.89	16.21	8.9
445	12.46	15.76	17.17	9.0
447	12.55	16.77	18.29	9.0
449	12.65	17.73	19.33	9.0
451	12.75	18.77	20.47	9.1
453	12.85	19.70	21.50	9.1
455	12.94	20.67	22.57	9.2
457	13.04	21.67	23.68	9.3
459	13.15	22.81	24.92	9.2
461	13.25	23.86	26.08	9.3
463	13.35	24.92	27.26	9.4
465	13.45	25.88	28.31	9.4
467	13.55	26.77	29.33	9.5
469	13.65	27.84	30.30	8.8
471	13.75	28.89	31.15	7.8

[a]From experimental TG data; [b]Estimated using vapor pressure data taken from [25] inserted in Eq. (1)
[c][(Predicted–Experimental)/Experimental]·100

However, if the system attains equilibrium quite rapidly during heating, the vaporization enthalpy can be alternatively obtained by nonisothermal TG data. The $\Delta_{vap}H$ value is determined from the slope of the lnα *vs.* T^{-1} regression line (Eq. (2)) after that the extent of vaporization (α), which is equal to $P/P°$ only if this assumption is valid, is determined as a function of temperature. The mentioned α *vs.* T dependencies for acetanilide at different heating rates are shown in Fig. 1. The slopes, intercepts (with the associated uncertainties) and squares of the correlation coefficients (R^2) are reported in Table 2. The derived vaporization

Table 2 Regression parameters of Eq. (2), vaporization temperatures and enthalpies of acetanilide determined from the TG data at different heating rates β. For comparison purpose, $\Delta_{vap}H$=69.6±0.8 kJ mol^{-1} was selected from the slope of the log(P/kPa) *vs*. $1/T$ plot (R^2=0.9999) obtained using the vapor pressure data taken from Eq. (3) over the same temperature range

β/K min^{-1}	$\ln\alpha = a+b(10^3/T)$			T_{vap}/K**	$\Delta_{vap}H$/kJ mol^{-1**}
	$a\pm\sigma_a$*	$-b\pm\sigma_b$*	R^2		
1	17.90±0.37	8.57±0.16	0.9931	479±2	71±2
2.5	17.37±0.38	8.57±0.18	0.9920	494±2	71±2
5	16.04±0.69	8.37±0.33	0.9708	521±2	70±3
10	16.06±0.56	8.61±0.28	0.9808	536±2	72±3

*standard deviation (N=21 for all experimental data)
**the associated uncertainties are determined as the sum of regression and measurements contributions

Table 3 Regression parameters of Eq. (2), vaporization temperatures and enthalpies of the studied acetanilide herbicides determined from the nonisothermal TG data carried out at 1 K min^{-1}

Compound	$\ln\alpha=a+b(10^3/T)$				T_{vap}/K**	$\Delta_{vap}H$/kJ mol^{-1**}
	$a\pm\sigma_a$*	$-b\pm\sigma_b$*	N	R^2		
alachlor	21.81±0.09	10.25±0.04	34	0.9995	470±2	85±1
metolachlor	17.61±0.10	8.43±0.04	34	0.9992	479±2	70±1

*standard deviation
**the associated uncertainties are determined as the sum of regression and measurements contributions

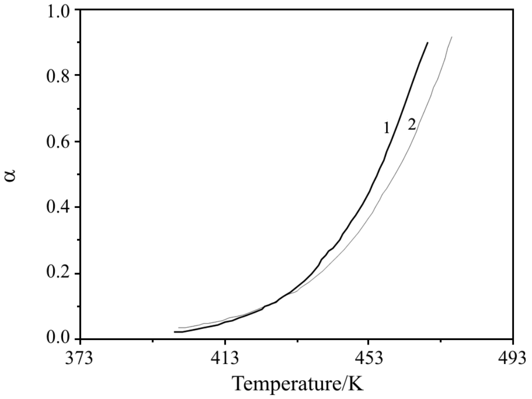

Fig. 2 α *vs*. T plot at 1 K min^{-1} for 1 – alachlor, 2 – metolachlor

temperatures and enthalpies are also listed in Table 2. An increasing trend is shown for the T_{vap} values, while the agreement of the $\Delta_{vap}H$ values is excellent. In order to test the reliability of the results these values were compared with the one selected from vapor pressure data of Eq. (3) using an approximated Clausius-Clapeyron relationship. In fact, since the experimental temperature range covers a significant narrower interval (from 401 to 471 K) the first two terms of Eq. (3) only can be considered. From the slope of the linear log$P$ *vs.* T^{-1} equation the vaporization enthalpy, $\Delta_{vap}H$=69.6±0.8 kJ mol^{-1} was selected (R^2=0.9999). This value is in close agreement with those obtained using Eq. (2), thus demonstrating the validity of this thermogravimetric method.

The α *vs.* T dependencies for alachlor and metolachlor derived from nonisothermal TG experiments carried out at 1 K min^{-1} are shown in Fig. 1. The regression parameters of Eq. (2) and their uncertainties are reported in Table 2 together with their very high R^2 values. The selected vaporization temperatures and enthalpies (with the associated uncertainties) for the acetanilide herbicides studied are reported in Table 2. Being these values obtained in the same experimental temperature range a simple comparison of the vaporization enthalpies enable to evidence the higher stability of alachlor with respect to metolachlor, which confirms the results obtained in a previous investigation [24].

Conclusions

Taking into account the validity of the thermogravimetric methods considered in this study to determine vapor pressure and vaporization enthalpy, the following results can be evidenced. First, the knowledge of the diffusion coefficient is required to select reliable mass loss rates to apply the Langmuir equation from experimental TG data. Second, to overcome this difficulty a simple nonisothermal TG method, which is based on the application of the Clausius-Clapeyron equation, can be applied to derive rapid and reasonable vaporization enthalpies using short experimental times, simple experimental set-up and small amount of sample.

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